

Explosives, Matches and Fireworks

by Joseph Reilly

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This book was undated but was printed about 1940. It is for the advanced chemist, which you may become if you apply yourself. Its tests and analysis of materials in explosives will give you the theoretical knowledge you will need to be an explosives manufacturer.

I eliminated the hundreds of distracting and irrelevant footnotes, referring to books printed in the 1930s back through the last century since they are unavailable.

EXPLOSIVES

MOST explosives consist either of a mixture of carbon compounds with compounds rich in oxygen, or of organic compounds such as nitro-compounds and nitric esters, which contain the oxygen necessary for their combustion. A smaller class of explosives includes substances which undergo exothermic decomposition. The materials to be tested comprise oxidising agents such as nitrates and chlorates, reducing agents such as carbon, sulphur and organic compounds; nitro-compounds, nitric esters and the raw materials required for their manufacture, solvents, stabilisers, and a variety of other ingredients. The increasing use of non-volatile solvents, such as centralite, and the production of smokeless, non-flash and non-hygroscopic explosives has extended the range of analytical tests in the examination of explosives.

This section deals mainly with chemical and stability tests.

A. INGREDIENTS AND RAW MATERIALS

I. NITRATES

(a) Potassium Nitrate

Mol. wt., 101.1; sp. gr., 2.109; M.P., 337°; decomp. at 400°; soluble in 100 parts water, 13.2 at 0°, 24.6 at 100°.

The nitre which reaches explosives factories is usually refined. For crude nitre see Vol. II., p. 420.

Moisture. A weighed quantity is heated in a platinum crucible until it just melts, cooled in a desiccator and again weighed. The moisture should not as a rule exceed 0.05 per cent. Limits ranging from 0.03 to 0.25 per cent. are specified in different countries.

Insoluble in Water. This is determined in the usual way and should be practically nil.

Chlorides. A qualitative test with silver nitrate is usually sufficient. If necessary, the turbidity is compared with that produced by a known amount of chloride. Specification limits vary from 0.005

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to about 0.03 per cent. For the quantitative estimation, the silver chloride may be weighed, or the chloride may be determined by titration with silver nitrate, using potassium chromate as indicator.

Sulphates. These are estimated as barium sulphate and should not exceed 0.1 per cent. (as K_2SO_4).

Perchlorates. These may be present in appreciable quantity in conversion-salt-petre. The following method gives very accurate results: 20 g. of the sample is heated to 545° in a covered nickel crucible and maintained for an hour at this temperature in a Gilbert furnace or electric furnace, to reduce the perchlorate to chloride, which is then titrated with silver nitrate by Mohr's or Volhard's method. The chloride present in an unheated sample is deducted. Any chlorate or iodate present must also be allowed for. Lenze recommended heating for half an hour in a porcelain crucible at 580° to 600°. The first quarter of an hour is occupied in raising the temperature to the required point. At higher temperatures losses of chloride occur.

Methods involving the addition of iron filings, manganese dioxide, sodium bicarbonate, etc., have been proposed, but appear to have no appreciable advantage. Leimbach has proposed a wet method depending on precipitation with nitron, after removing the nitrate and chlorate by heating with hydrochloric acid. Reduction of the perchlorate with titanous sulphate has also been recommended.

Specification limits from 0.1 to 0.3 per cent. are given; potassium nitrate containing nitrites under 0.5 per cent. did not increase the sensitiveness of gun-powder and synthetic nitrates were found to be as suitable as material prepared from Chili nitrates.

Chlorates. Traces of chlorate give a yellow colour when the salt-petre is added to concentrated sulphuric acid. This can be used roughly as a colorimetric method. Another sensitive test depends upon the formation of a blue colour by aniline hydrochloride in concentrated hydrochloric acid. Chlorates can also be reduced to chloride by zinc, iron, formaldehyde, sulphurous acid, etc. The

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chloride is then determined by filtration. In most specifications chlorates are excluded entirely. Sometimes 0.01 per cent. is admitted.

Salt-petre is also tested for carbonates, sodium, calcium and magnesium salts, and nitrites. These should be practically absent.

Potassium nitrate which is made from synthetic nitric acid, either by direct neutralisation with potassium carbonate, or through the sodium salt, is very pure and in general it suffices to test for moisture, insoluble matter, chloride and chlorate.

The moisture content is generally less than 0.1 per cent. and the impurities are present only in traces.

Estimation of Potassium Nitrate. Potassium nitrate is readily determined in gun-powder and allied mixtures by extraction with water. The nitrate may be determined, if necessary, by means of the Lunge nitrometer, or by precipitation with nitron.

(b) Sodium Nitrate

Mol. wt., 85.0; sp. gr., 2.26; M.P., 312°; soluble in 100 parts water, 73 at 0°, 175 at 100°; slightly soluble in alcohol.

The requirements of sodium nitrate for the manufacture of nitric acid are given in Vol. I., p. 470. Sodium nitrate for explosive purposes may be tested for moisture, insoluble matter, potassium, calcium, chloride, sulphate and sometimes iodide, iodate and perchlorate. The methods are in general similar to those for potassium nitrate. Sodium nitrate is now largely made from synthetic nitric acid. This gives a comparatively pure product, which may, however, contain small quantities of nitrite, chloride and soda. The nitrite may be tested for in small quantities by potassium iodide and starch, the estimation being made colorimetrically. Larger quantities may be estimated by titration with potassium permanganate.

(c) Ammonium Nitrate

Mol. wt., 80.0; sp. gr., 1.725; M.P., 169.6°; decomp. at about 200°; soluble in 100 parts water, 118 at 0°, 870 at 100°; slightly soluble in alcohol.

This salt is used very extensively in explosives. Owing to a number of disasters with ammonium nitrate explosives a great

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amount of research has been carried out on the use of this substance alone and in mixtures for explosive use. The material should be white or very slightly grey or yellowish. It should give a clear solution in water. The size of particles is generally specified. The moisture is estimated by drying in a vacuum over sulphuric acid for

at least twenty-four hours; if it is necessary to shorten the time by warming, the temperature should not exceed 70°.

Oils are sometimes present, being added to reduce the hygroscopicity. These may be estimated by extraction with ether or benzene. Nitrite should be absent, and there should be practically no acidity to methyl orange.

Pyridine and thiocyanate may be present in ammonium nitrate made from gas-works ammonia and should be avoided as far as possible.

Thiocyanate is estimated colorimetrically. Ammonium nitrate made from sodium nitrate by double decomposition practically always contains sodium salts. The total ammonium nitrate content is determined by estimations of the ammonia and nitrate by the usual methods.

(d) Barium Nitrate

Mol. wt., 261.4; sp. gr., 3.23; M.P., 592°; soluble in 100 parts water, 5.0 at 0°, 34.2 at 100°.

Barium nitrate is used in certain explosives such as tonite, and in firework mixtures. It is tested for moisture, insoluble matter, neutrality, chloride, chlorate, sodium, calcium, and lead. On addition of slight excess of sulphuric acid and filtering, the solution should give only traces of residue after evaporation and ignition. The total barium is estimated by the usual methods. The nitrate is best estimated by reduction to ammonia. Barium nitrate may be readily estimated in mixed explosives by extraction with water and precipitation with sulphuric acid.

(e) Lead Nitrate

Mol. wt., 331.0; sp. gr., 4.41; decomp. at about 200°; soluble in 100 parts water, 36.5 at 0°, 127 at 100°; slightly soluble in alcohol.

Lead nitrate should dissolve in water without residue. On adding sulphuric acid, and filtering, the liquid should give practically no residue on evaporation and heating. Impurities are tested for as in barium nitrate.

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II. CHLORATES AND PERCHLORATES

(a) Potassium Chlorate

Mol. wt., 122.55; sp. gr., 2.34; M.P., 370°; decomp. slightly above M.P.; soluble in 100 parts water, 3.3 at 0°, 56 at 100°; slightly soluble in alcohol.

Potassium chlorate should be pure white, free from smell and in a very fine crystalline condition. The degree of fineness is usually specified. The purity of the salt is important for explosive purposes, as impurities may lead to increased sensitiveness to shock and friction. The moisture is usually restricted to 0.2 to 0.5 per cent.

The aqueous solution should be neutral, and should give only traces of insoluble matter; gritty matter such as sand is particularly to be avoided. The potassium chlorate should be practically free from chloride, perchlorate, nitrate, sulphate, carbonate and lead. Sodium, calcium and arsenic are sometimes tested for. Organic matter should be absent.

Bromate frequently occurs in appreciable proportions up to 0.5 per cent. and is to be avoided. It gives a blue colour with potassium iodide and starch in presence of dilute sulphuric acid; chlorite and hypochlorite also react with starch iodide. Chlorate gives a similar coloration on longer standing. The bromate may be estimated quantitatively by addition of potassium iodide and dilute acid, and titrating back the free iodine with thiosulphate. Specification limits vary from 0.05 to 0.15 per cent.

Nitrates may be tested for by evaporating with a solution of brucine and oxalic acid in alcohol; the presence of nitrate is indicated by a red colour.

Perchlorate is detected by addition of a 0.3 per cent. solution of methylene blue, which gives a violet precipitate with green fluorescence.

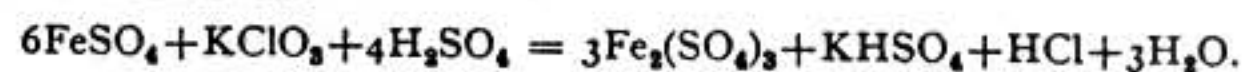
Estimation of Chlorate. The total chlorate may be estimated as

follows, and should be at least 98.5 to 99 per cent.

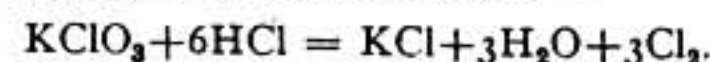
(a) By ferrous sulphate. The chlorate solution is placed in a flask fitted with a Bunsen valve. A solution of 100 g. ferrous sulphate crystals and 100 c.c. conc. sulphuric acid in a litre of water is prepared, and 25 c.c. of this is added to the flask and boiled for ten minutes. After cooling, the excess of ferrous salt is titrated back with *N*/2 permanganate. It is desirable to add some manganous sulphate, as the hydrochloric acid formed may otherwise give rise to difficulty.

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It is also recommended to titrate slowly. The reaction which takes place is as follows:—



(b) Iodometric method. The chlorate is heated with excess of hydrochloric acid, and the gas evolved is passed into excess of potassium iodide solution. The reaction is as follows:—



The chlorine exists partly as lower oxides, but this does not affect the amount of iodine liberated. The chlorate is weighed and placed in a flask. Fuming hydrochloric acid is added, and the flask is quickly connected to the tube passing to the potassium iodide solution (1:10). After boiling off the chlorine, an excess of *N*/10 thiosulphate is added to the iodide solution and titrated back with iodine solution, using starch as indicator.

Other methods depend upon reduction of the chlorate with sulphurous acid, iron, etc., and estimation of the chloride formed, and upon precipitation as nitron chlorate. Methods for the detection of small quantities of chlorate have been given under potassium nitrate.

(b) Sodium Chlorate

Mol. wt., 106.45; sp. gr., 2.49; M.P., 248°; soluble in 100 parts water, 82 at 0°, 204 at 100°; soluble in alcohol.

Sodium chlorate is deliquescent and is relatively little used. It may be tested in the same way as potassium chlorate. Roman gives the following specification: sodium chlorate 99.5 per cent., sodium chloride 0.2, bromide 0.1; traces of heavy metals and alkaline earths; no mechanical impurities; no insoluble residue in water.

(c) Potassium Perchlorate

Mol. wt., 138.55; sp. gr., 2.52; M.P., 610°; soluble in 100 parts water, 0.7 at 0°, 18.7 at 100°.

Potassium perchlorate forms a white, crystalline solid, which is very sparingly soluble in water. It is not hygroscopic. It should be in a fine state of subdivision. It is much more stable than the chlorate; it is not readily decomposed by acids, and is reduced with difficulty in solution. It should be free from sodium salts.

Chlorides and sulphates should be present only in small proportion. Chlorate should be present only in traces. This may be tested

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for qualitatively by warming with hydrochloric acid. A smell of chlorine indicates the presence of chlorate. The chlorate may be estimated colorimetrically by the yellow-brown colour produced on warming with hydrochloric acid and potassium iodide.

Potassium perchlorate may be detected in mixtures by the methylene blue reaction (see under Potassium Chlorate). It may be estimated quantitatively by heating, as described under Potassium Nitrate, or by nitron; also by precipitation as methylene blue perchlorate and titration of the excess of methylene blue with picric acid. It can also be reduced with titanous sulphate or chloride.

Sodium perchlorate contains a higher proportion of oxygen, but is not suitable for use on account of its hygroscopicity.

(d) Ammonium Perchlorate

Mol. wt., 117.45; sp. gr., 1.87; soluble in 100 parts water, 12.4 at 0°, 88.2 at 100°; slightly soluble in alcohol and acetone.

The examination is similar to that of the potassium salt. Absence of chlorate is of special importance. Chlorides and sulphates should not exceed about 0.5 per cent., ash 0.5 per cent., and moisture 0.25 per cent. The ammonium perchlorate content should be at least 99 per cent.

III. INGREDIENTS OF GUN-POWDER

(a) Potassium Nitrate (see p. 1).

(b) Sulphur

At. wt., 32.06; sp. gr., 2.06 (rhombic); melts at 112-119°; boils at 444.5°; insoluble in water; soluble in many organic solvents, especially carbon disulphide (100 parts dissolve 37 parts sulphur at 15°).

For explosive purposes finely powdered roll sulphur is used. It must be free from acid. The moisture is estimated by drying in a vacuum or by warming, but a temperature of 70° should not be exceeded. The loss of weight should not be more than 1 per cent. The residue on burning off the sulphur should not exceed 0.15 per cent. Some specifications permit up to 0.5 per cent. The residue should be free from sand.

Arsenic is indicated by a bright yellow or reddish colour, and may be estimated by warming 5 g. of sulphur with 100 c.c. ammonia to 50°-60° for fifteen minutes, filtering, acidifying the liquor, and treating

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with hydrogen sulphide. There should be no weighable precipitate. Alternatively, a titration method with silver nitrate and potassium chromate may be used.

Sulphur may be extracted from mixtures by freshly distilled carbon disulphide. It may be determined by evaporating at least three times with strong *aqua regia* to convert it to sulphuric acid, and precipitating with barium chloride.

(c) Charcoal

The examination is mainly physical. Good charcoal should have a deep black, velvety fracture, low density, and should be soft and easily rubbed to powder. It should not scratch copper and should ring well when struck. Charcoal from different woods may be recognised by the pith, which is round and brown for dogwood, black and round for willow, triangular for alder, and small, round and black for hazel wood. Birch and poplar are also sometimes used. Brown charcoal is recognised by its colour. The moisture is estimated by heating at 100° and should not exceed 4 per cent. The carbon content is sometimes determined, and ranges from about 70 to 75 per cent. The ash is determined in the usual way. It should not contain gritty matter.

IV. VARIOUS INGREDIENTS

(a) Graphite

Graphite is used for coating powders. It must give an adherent, uniform coating and for this purpose must be very finely ground. It should have a uniform grey colour, and a smooth feel when rubbed. Pure graphite has a specific gravity of 2.255. It should be free from acid. The ash is determined in the usual way, but vigorous heating is necessary to burn off the graphite. The residue may amount to 15-25 per cent. Silicates should be absent. Volatile matter is estimated by heating in an atmosphere of nitrogen. The carbon content may be estimated by combustion in a current of oxygen, and determination of the carbon dioxide. Sulphur is determined by heating with magnesia and sodium carbonate, then with ammonium nitrate or sodium peroxide to convert to sulphate, which is estimated as barium sulphate.

(b) Aluminium

At. wt., 27.0; sp. gr., 2.70; M.P., 658°.

Aluminium is used in a finely powdered condition or as flake in explosive mixtures. The degree of fineness and bulk density are

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usually specified. The aluminium must be as free as possible from oxide and from impurities which promote oxidation on storage. The specification limits for aluminium content range from about 92 to 98 per cent. Iron is frequently present up to 0.5 or 1 per cent., and small quantities of zinc and copper are met with (0.1 to 0.2 per cent.). The copper content should be as low as possible, since larger amounts make the aluminium very reactive towards nitrates. Silicon is also found up to about 0.5 per cent. Oily matter is often present up to 0.3-0.5 per cent. Soap should not be present in more than very small proportions. The loss of weight on heating to 100° for an hour should not exceed 0.25 per cent. For the determination of the aluminium content, the metal is dissolved in hydrochloric acid or potassium hydroxide solution, and the hydrogen evolved is measured, or determined by a gravimetric method. Other methods depend upon reduction of ferric sulphate, and on conversion of the aluminium to chloride which is then distilled off in a current of hydrogen chloride.

(c) Magnesium

At. wt., 24.32; sp. gr., 1.74; M.P., 650°.

Magnesium is used in a powdered form. The degree of fineness is usually specified. The magnesium should be as free as possible from oxide and from other metals. Small quantities of iron are usually present (0.5 to 1 per cent.). Copper, aluminium, manganese, zinc, lead, calcium and silicon may be present in traces. Gritty matter is to be avoided, and oil or fat should be present only in traces. The content of metallic magnesium is estimated by measuring the hydrogen evolved on treatment with hydrochloric acid (*cf.* aluminium).

(d) Paraffin Wax

This should be white and as transparent as possible. It should have no taste or smell. It must be free from mechanical impurities and acidity, and must dissolve completely in acetone or carbon disulphide. On ignition it should give very little ash. The melting point is not very definite. It is generally specified for the special purpose for which the paraffin wax is required. The determination of the setting point is sometimes preferred.

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The apparatus for this test consists of a thermometer of suitable range and a small glass cup with a hole in the bottom. About 0.2 g. of the paraffin or mineral jelly is placed in the cup, which is then fitted on to the bottom of the thermometer bulb. On slowly heating the thermometer and cup, the temperature at which drops of melted paraffin fall away from the cup is noted.

(e) Colophony

This is a brittle, vitreous material of yellow to brown colour and sp. gr. 1.07 to 1.08. It has very little taste or smell. It is insoluble in water, but dissolves in alcohol and most other organic solvents. It has a very indefinite melting point. On heating it softens at 70° and becomes molten at about 108°. It should not lose more than 0.2 per cent. on heating at 100°.

(f) Castor Oil

Castor oil is used to reduce the sensitiveness to friction. It is also a waterproofing agent and prevents the recrystallisation of potassium chlorate. The oil is colourless or pale yellow, highly viscous, and somewhat lighter than water (sp. gr. 0.96 to 0.97 at 15°). It is optically active and has a refractive index of 1.4773. It is miscible with absolute alcohol and many other organic solvents, but is insoluble in petroleum-ether and benzene, and incompletely soluble in 90 per cent. alcohol. A mixture of 10 c.c. of the oil and 50 c.c. of alcohol of sp. gr. 0.829 at 17.5° should give no turbidity. On shaking with an equal volume of 50 per cent. nitric acid it should not blacken. The acidity is determined by dissolving in alcohol and titrating with alkali. The saponification number is estimated in the usual way. Colophony

can be detected by dissolving in acetic anhydride and adding a drop of concentrated sulphuric acid (violet or red colour). Paraffin wax may be detected by saponifying 5 g. of the oil with 20 c.c. of a solution of 40 g. sodium hydroxide in 93 c.c. water and 500 c.c. glycerol. The hot liquid is then added drop by drop to 50 c.c. of methyl alcohol. In absence of paraffin wax the liquid remains clear on cooling; 2 per cent. of wax causes the liquid to become cloudy, and after a time gelatinous. The refractive index and viscosity are also made use of to ensure absence of impurities.

(g) Kieselguhr

Kieselguhr is used for the manufacture of dynamite. It consists of diatoms which are capable of absorbing considerable quantities of nitroglycerine or other liquids. It is obtainable commercially in

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fairly pure condition, but is subjected to calcination at the dynamite factory before mixing with the nitroglycerine. It should be white or faintly reddish and should have a smooth feel when rubbed between the fingers. It should be as free as possible from sand, acid, and organic matter. The water content should not exceed 1 per cent. Sand may be separated by shaking with water and allowing to settle quickly. The separation is facilitated if the kieselguhr is first broken down by boiling with strong alkali. The absorptive capacity is ascertained by mixing weighed quantities of nitroglycerine and kieselguhr, filling into a cavity in a wooden block and pressing with a wooden plunger by means of a definite weight. The lower end of the cavity is open and is covered with a piece of parchment paper. The amount of nitroglycerine which is pressed out is an inverse measure of the absorptive capacity. A rough indication is also given by the amount of nitroglycerine necessary to make the kieselguhr appear wet; a good kieselguhr should take up at least four parts.

(h) Wood Meal

Wood meal should be free from acid and foreign substances, especially sand and metallic particles. No chemicals should be used in the manufacture, and bleaching agents should be avoided. The degree of fineness is generally specified. Larger fragments of wood should not be present.

Limits for the moisture content range from 5 to 10 per cent. The ash should not exceed 0.5 to 1.0 per cent. Resin is determined by extraction with ether. Extraction with alcohol removes tannin, etc. These extracts should be very small in quantity. Wood meal contains small quantities of water-soluble matter, which should be taken into account in the estimation of wood meal in dynamite, etc.

The cellulose content may be estimated by treatment with caustic soda and chlorine.

Wood meal should absorb liquids readily. Thus it should retain 60 to 70 per cent. of nitroglycerine without exudation. The combustibility is tested by mixing one part of wood meal with 3 parts of potassium nitrate and burning in a lightly covered crucible. The residue should not exceed 10 per cent. The rapidity of burning is measured by filling some of the mixture into a groove in a sheet of metal and igniting at one end.

The bulk density is measured by adding the wood meal little by little to a 100 c.c. measuring cylinder, which is knocked on the table after each addition to shake the wood meal down. The quantity which fills 100 c.c. is weighed.

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Wood meal may be detected in mixtures by the microscope or by the phloroglucinol test. One gram of phloroglucinol is dissolved in 15 c.c. of alcohol, and 10 c.c. of syrupy phosphoric acid is added. A little of the meal is rubbed with 0.5 c.c. of this reagent in a porcelain dish. Wood fibres show a rose colour changing to carmine. Apart from wood meal other forms of meal (corn, potato) are similarly used.

(i) Chlorides, Oxalates, Carbonates

Sodium and potassium chlorides are much used in industrial explosives. They are generally obtainable in a sufficiently pure condition. They should be free from hygroscopic impurities. The degree of fineness is of importance and is generally specified; large particles should not be present.

The oxalates of potassium, sodium, and ammonium should be pure white, and free from mechanical impurities. The two former should be free from acidity and alkalinity; ammonium oxalate may develop slight acidity by hydrolysis and the litmus paper tends to change colour on drying. The sodium salt is anhydrous, the two others have water of crystallisation. They should dissolve practically completely in water and should be free from chlorides, sulphates and heavy metals. The ammonium salt should leave no residue on ignition. Oxalates are readily detected as the calcium salt and the purity can be determined by titration with permanganate.

Sodium carbonate is occasionally used as a stabiliser in blasting explosives. It should be of 98 to 99 per cent. purity, and should contain only traces of chlorides, sulphates, and ammonia. It should dissolve in water without residue.

Sodium bicarbonate should be finely powdered, and should dissolve completely in water. Carbonates of other metals should be present only in traces, and chlorides and sulphates should also be practically absent. The purity should be at least 99 per cent.

Calcium carbonate should be in a very finely dissolved condition; the state of subdivision is usually specified. It should be practically free from calcium oxide or hydroxide and from salts of metals other than calcium.

(j) Cuprene

For gun-powder required for burning under reduced pressure, Grimwood recommends the use of cuprene, a polymerised product from acetylene. This may be used to replace either wholly or in part the charcoal of gun-powder. Even at very low pressures the rates of burning are not appreciably altered when this substance is used.

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V. STABILISERS

(a) Camphor

$C_{10}H_{16}O$; mol. wt., 152.1; sp. gr., 0.985 at 18°; M.P., 180°; B.P., 209°; soluble in water 0.1 per cent.; soluble in organic solvents.

Apart from natural camphor, the synthetic material is now made in considerable quantities. Natural camphor is optically active, the synthetic product is the racemic form, and is inactive except for small quantities of impurities.

On heating, camphor should not begin to sinter below 173° and should not melt below 175°. On sublimation it should leave practically no residue (0.1 per cent.). It is tested for acid by dissolving in alcohol, precipitating with water and testing the solution. The presence of water is indicated by turbidity on dissolving in petroleum ether. Camphor gives a yellow to brown solution in concentrated sulphuric acid, according to the organic impurities present.

Crane and Joyce recommend for the determination of the purity of camphor—

- (1) Determination of residue on sublimation.
- (2) Sp. gr. of a 10 per cent. solution in benzene.
- (3) Optical rotation (for natural camphor).

(b) Diphenylamine

$(C_6H_5)_2NH$; mol. wt., 169.1; sp. gr., 1.159; M.P., 54°; B.P., 302°; practically insoluble in water; soluble in most organic solvents.

The compound should be white or pale yellow. It should melt at 52° to 54° and should yield practically no insoluble residue in ether or alcohol. It should also give a clear solution in pure sulphuric acid (a blue colour indicates the presence of nitrate). It should have no unpleasant smell. Aniline bases should be present only in traces (0.001 per cent.). These may be tested for by bleaching powder.

In the detection of diphenylamine the nitric acid reaction is used. The quantitative estimation is described under Smokeless Powder (p. 53).

(c) Substituted Ureas

Symmetrical diethyl- and dimethyldiphenyl-urea are known as Centralite I and II respectively. They are used as stabilisers, as they absorb the oxides of nitrogen, formed by the decomposition of nitric esters.

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Centralite I melts at 79° and Centralite II at 121.5°. They sublime above the melting point. They are very sparingly soluble in water, but dissolve readily in alcohol and ether. They should be almost colourless and free from aniline, volatile substances, chlorides and mechanical impurities. They should give clear solutions in alcohol and should give no residue on incineration.

Asymmetric diphenylurea (acardite) also belongs to this class of compounds. It melts at 189°. On boiling with sodium hydroxide solution it is hydrolysed to diphenylamine which can be driven over by steam. The symmetrical derivative melts at 235°. It is not volatile in steam.

Substituted urethanes are also used as stabilisers.

The estimation of centralite, etc., is dealt with under Smokeless Powders (p. 53).

(d) Mineral Jelly

This is used principally for the manufacture of cordite. It should be free from foreign matter, scales and particles, and should have a flash point of at least 400° F. (205° C.) and a sp. gr. of not less than 0.87 at 100° F. (37.8° C.). It should not lose more than 0.2 per cent. in weight on heating for 12 hours on a water-bath and should be practically free from mineral matter. The acidity may be tested by dissolving in ether, allowing to settle and titrating a measured portion of the liquid with alcoholic potassium hydroxide. The mineral jelly should be practically neutral. Mineral jelly has no definite melting point. It is important that the mineral jelly shall not have been melted for two or three days before testing.

Mineral jelly is practically insoluble in a mixture of 4 parts methyl alcohol and 1 part water, and this is made use of in the separation of mineral jelly from nitroglycerine, etc.

Camphor, substituted ureas and triphenyl phosphate are sometimes used to modify the rate of burning of gun-powder. Phthalides are claimed to have advantages over centralite in certain smokeless powders.

VI. NITRATION ACIDS

(a) Nitric Acid

The methods of testing are given in Vol. I., p. 489. These include the total acidity, lower oxides of nitrogen, sulphuric acid, chlorine, iodine and mineral matter. The lower oxides are usually restricted

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to 1 per cent. (as NO_2). Chlorine should not exceed 0.03 per cent. and mineral matter 0.01 per cent. Nitric acid may contain traces of tetranitromethane and of chloronitromethanes, which are liable to find their way into nitroglycerine and lower the heat test.

(b) Sulphuric Acid and Oleum

Methods of testing are given in Vol. I., pp. 416, 456.

(c) Mixed Acids and Spent Acids

Mixed acids for nitroglycerine manufacture should be as free as possible from suspended matter, such as sulphates of iron or lead, as these may delay the separation.

In the spent acids the nitric acid content is lower and the water content higher than in fresh mixed acids. They also contain organic matter which differs according as the acids are from nitrocellulose,

nitroglycerine, or nitroaromatic compounds. The presence of these and of muddy suspensions gives rise to some difficulties in analysis. In the determination of nitrogen by the nitrometer method allowance must be made for dissolved nitroglycerine; this may be determined by extraction with ether or chloroform and evaporating gently. The estimation of nitrous acid may also be affected by organic matter. Raschig avoids this by adding potassium iodide and titrating the liberated iodine in an atmosphere of carbon dioxide.

Webb gives the following method for the waste acid from nitroglycerine manufacture: A sample is maintained at 120° in a calcium chloride bath for 20 minutes, and the nitric acid is driven off by a current of steam. The residual solution contains sulphuric and oxalic acid. The latter is estimated by titration with permanganate at 60° and the sulphuric acid is determined by titration with alkali and methyl red after addition of 1 c.c. of 3 per cent. hydrogen peroxide for each 5 c.c. of permanganate previously used up. This is to destroy organic matter. It is necessary to calculate from the permanganate titration the amount of sulphuric acid which is used up in the reaction between permanganate and oxalic acid and to add this to the sulphuric acid estimated by the alkali titration. The nitric acid is determined by Lunge's method. Dissolved nitroglycerine is oxidised by potassium bichromate, and the excess of bichromate estimated by potassium iodide and thiosulphate.

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VII. CELLULOSE

(a) Cotton Cellulose

The cotton cellulose used for the manufacture of nitrocellulose must be as free as possible from husks, seeds, paper, dust, coal, sand, woven and twisted masses, and must not contain residues of soda or bleach. It should not be acid. The moisture is determined by heating 5 g. at 103° to 105° to constant weight and may amount to 7 to 8 per cent. The ash should not exceed 0.5 to 1 per cent. Oily matter is determined by extraction with ether and is generally restricted to 0.4 to 0.6 per cent. Starch should be absent or present only in traces.

Alpha-cellulose. Ten g. of cellulose is broken down by kneading in a mortar with 50 c.c. of 17.5 per cent. sodium hydroxide solution free from carbonate. After 30 minutes 50 c.c. of water is added, and the cellulose is filtered and washed. The mass is wetted with hot dilute acetic acid, again washed, and dried. The residue represents the alpha-cellulose, after deducting the weight of the ash.

Reducing Substances. These are tested for by the "copper value." In the method of Schwalbe the cotton is boiled with Fehling's solution, prepared by adding copper sulphate solution to alkaline Rochelle salt. In Braid's modification, which is stated to give more consistent results, 2.5 g. of very finely divided air-dry cotton is treated with a mixture of 5 c.c. of 10 per cent. copper sulphate (cryst.) and 95 c.c. of an almost-saturated solution of sodium carbonate and bicarbonate (350 g. soda crystals and 50 g. bicarbonate made up to 1 litre). The cotton is immersed by means of a rod and the air bubbles are allowed to escape; the flask is then surrounded with boiling water for exactly three hours. The contents are filtered off on an asbestos filter and washed first with dilute sodium carbonate solution and then with water. Then the residual cuprous oxide is dissolved by treatment with a solution containing 100 g. of iron alum and 140 g. of concentrated sulphuric acid per litre. Two such treatments usually suffice. The filter is then washed with 2 N-sulphuric acid; the combined filtrate and washings are titrated with N/25 potassium permanganate solution. According to Brissaud the test is affected by air.

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Alkali-soluble Substances. The methods vary somewhat in detail. The following conditions are given by Landon. Five g. of dried cellulose is placed in a litre flask, and 300 c.c. of 10 per cent. potassium hydroxide solution (or the equivalent of sodium hydroxide) added. The hydroxides should be free from carbonate. The mixture is boiled under a reflux condenser for three hours. The ebullition should be as

regular as possible; fragments of porcelain may be added to prevent bumping, and should be removed afterwards. The mixture is poured into a litre of cold water; the flask is rinsed carefully and acetic acid is added to destroy combinations of cellulose and alkali. The cellulose is filtered, washed with hot water and dried. The loss of weight represents the alkali-soluble material. Landon gives a limit of 3 per cent. Part of the alkali-soluble material can be reprecipitated with acid. This is known as wood gum. The following method is in use: 15 g. of the dried cellulose is immersed in 300 c.c. of a 5 per cent. solution of sodium hydroxide, and allowed to stand for twenty-four hours at 18° to 20° with frequent shaking. The liquid is filtered off and 100 c.c. mixed with 200 c.c. of alcohol (92.5 per cent. by weight). A little phenol phthalein is added and then 9.5 c.c. of hydrochloric acid (1.19) to neutralise most of the alkali. The neutralisation is completed with normal acid, and a further 5 c.c. of acid is added. After twenty-four hours the precipitate is collected on a tared filter paper or in a Gooch crucible, washed with alcohol and ether, dried at 100° and weighed.

Cotton is also tested for ligneous matter by absorption of dyes (fuchsine, methylene blue, malachite green) and for the viscosity of its solution in cuprammonium liquor. Gabillion gives the following figures for various cottons:—

Moisture, 4.5 to 6.0; ash, 0.1 to 0.25; fats, 0.1 to 0.25 (maximum) 0.8; iron, 0.008; insoluble in H_2SO_4 , 0.1 to 0.5; alpha-cellulose, 99 per cent.; copper number (unbleached) 0.07 to 0.10, (moderately bleached) 0.1 to 0.2, (strongly bleached) 3 to 4; potash number, 2.

(b) Wood Cellulose

Wood cellulose which is to be converted to nitro-cellulose must be in a form in which it can be readily dipped into the nitration acids

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and must be highly absorbent to permit of the penetration of the acids. It should be practically free from acidity and alkalinity, and from any residual chlorine from the bleaching process.

The moisture is estimated by heating 5 g. of the cellulose to 103° to 105° to constant weight. It is desirable to dry the cellulose partially at a lower temperature, otherwise some charring may take place at 105°. The dried cellulose should be allowed to cool in a stoppered weighing bottle, as it reabsorbs moisture very readily. Limits of 6 to 8 per cent. are specified.

The ash is determined in the usual way, taking 5 to 20 g. of material and finishing at a dull red heat. If calcium sulphate is present in quantity, it may be reduced; in this case the cellulose may be first destroyed with nitric acid.

Fats and resins are determined by extraction with ether. Figures up to about 1 per cent. are given. Extraction with alcohol is sometimes also included. The method of determination of alpha-cellulose is given under Cotton (p. 16). Alkali dissolves xylan together with some oxycellulose, etc., and on neutralisation a mixture of substances is precipitated which is designated as wood gum. The method of estimation is given under Cotton Cellulose (p. 16). The figure obtained on neutralisation is known as the neutral wood gum number. Excess of acid gives a somewhat lower figure (acid wood gum). Figures of 5 to 8 per cent. are given for the neutral wood gum. It is to be observed that the precipitate readily carries down a considerable proportion of sodium chloride from solution; this should be estimated and deducted from the total.

Pentosans are estimated by conversion to furfural. This is effected by distillation with dilute hydrochloric acid. Oxycellulose and other constituents of wood cellulose are also stated to yield small quantities of furfural. Methyl pentosans similarly yield methyl furfural. The wood cellulose is distilled with 12 per cent. hydrochloric acid until no more furfural is evolved. The furfural is then determined by precipitation with phloroglucinol. This gives a phloroglucide which can be washed, dried, and weighed.

According to Heuser and Boedeker, furfural = (phloroglucide + 0.001) × 0.571, and pentosan = furfural × 1.375.

A more expeditious volumetric method is given by Powell and Whittaker. 0.5 to 0.8 g. of material is distilled with 12 per cent. hydrochloric acid until the distillate gives no more pink colour with aniline acetate. The apparatus used for the distillation should have all-glass connections. Into each of four well-stoppered bottles is

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pipetted 25 c.c. of standard sodium bromide-bromate (approx. $N/10$). To two of the bottles are added 200 c.c. of the above distillate, and to the others 200 c.c. of 12 per cent. hydrochloric acid. After standing for an hour in the dark, about 10 c.c. of 10 per cent. potassium iodide solution is added, and the iodine is titrated with $N/10$ thiosulphate. The difference between the blank and the test titration is a measure of the furfural. One g. mol. furfural is found to react with 4.05 g. atoms of bromine. According to Schwalbe, Kraftcellulose gives the highest pentosan content (7.6 to 9.3 per cent.); next comes unbleached soda cellulose with 5.9 to 7.7 per cent. Sulphite cellulose gives 3.3 to 4.6 per cent.

The copper value is used for the estimation of reducing substances (mainly oxycellulose). The method is given under Cotton Cellulose (p. 16). It is stated that pentosans and other constituents of wood cellulose also react to some extent. Hydrocellulose is formed by the action of acids on cellulose. On further hydrolysis with acid and neutralisation, it reduces Fehling's solution. Estimations of the hydrocellulose are not usually included.

Lignin presents considerable difficulties, as the constitution is unknown and definite quantitative reactions are not available. It contains hydroxy, acetyl, and methoxy groups. It can be acetylated and nitrated. Numerous colour reactions have been suggested. The commonest of these is the phloroglucinol reaction. A solution of 1 g. phloroglucinol in 50 c.c. alcohol is mixed with 25 c.c. conc. hydrochloric acid. This gives a red colour with lignin. It is important that the solutions be freshly mixed. It is sometimes specified that the cellulose shall not give more than a faint rose colour. Another test in common use is to dissolve 0.02 g. wood cellulose in 5 c.c. of conc. sulphuric acid and allow to stand for an hour. This gives a brown colour.

The determination of the methoxy-group by the Zeisel method is sometimes used as a quantitative test, but the reaction is also given by methyl pentosans.

The wood cellulose may also be examined for viscosity in cuprammonium solution. To ascertain whether wood cellulose absorbs nitration acids readily, about 1 g. is pressed together lightly by hand and thrown on to a mixed acid containing 20 to 25 per cent. nitric, 70 to 60 per cent. sulphuric and 10 to 15 per cent. water. The cellulose should sink within one minute. On nitration it should neither become pappy nor become stiff through parchmmentising. The following limits

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are given by Scharrnbeck. With the exception of the moisture estimation the percentages are calculated on the dry material:—

	Per cent.
Moisture	7.0
Ash	0.6
Wood gum (sulphite cellulose)	5.0
„ „ (soda cellulose)	6.0
Chlorine—faint opalescence with $AgNO_3$
Alkali—faint red colour with phenolphthalein
Soluble in alcohol	0.5
Lignin—faint red with phloroglucin reagent

VIII. POLYHYDRIC ALCOHOLS

(a) Glycerine

Glycerol, $C_3H_8(OH)_3$; mol. wt., 92; sp. gr., 1.262; B.P., 290°; miscible with water and alcohol; insoluble in ether.

Pure glycerine is a colourless viscous liquid. The commercial product as used for dynamite is yellow to brownish in colour, and

has usually a faint caramel-like odour when rubbed between the hands.

According to Crosfield glycerine for explosives manufacture must be a distilled product as free as possible from water and containing at least 98 per cent. glycerol. Its specific gravity should be not less than 1.262 (15.5°/15.5°). It should be free from lead, calcium, fatty acids, sugars and decomposition products of glycerol (acrolein, etc.) and should not contain more than traces of arsenic, iron and chlorides.

The glycerol content may be determined, if required, by acetylation, or by oxidation with dichromate.

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The water content may be approximately estimated by heating in a weighing bottle with a loose stopper at 90°. Some evaporation of glycerol takes place; the heating should be continued until the successive losses are very small and approximately constant. The total loss is corrected for the loss of glycerol. Distillation with trichloroethylene has also been proposed.

Reducing substances may be detected by addition of silver nitrate and allowing to stand in the dark for fifteen minutes; Fehling's solution should give no reduction on standing for twelve hours in the dark.

The organic and inorganic residues are determined by gradually evaporating 25 g. and completing the evaporation in an air bath at 160°. A little water should be added to the residue from time to time to prevent it from becoming too thick. The residue is weighed, and then ignited to ascertain the percentage of ash. The former should not exceed 0.25 and the latter 0.05 to 0.10 per cent.

Acidity and alkalinity are tested for in the usual way, after diluting the glycerine with two volumes of water. The glycerine should be practically neutral.

Fatty acids are estimated by diluting with an equal volume of water, extracting with ether, washing the ethereal solution several times with water, evaporating off the ether, and drying at 70°. No more than traces should be present.

For the determination of saponifiable matter, 100 g. of the sample is weighed out in a flask, 200 c.c. of boiled distilled water and 30 c.c. of *N/1* sodium hydroxide are added; the whole is maintained at 100° for an hour and titrated.

Sugar and gums are shown by darkening on shaking with concentrated sulphuric acid. Small quantities of polyglycerines may be present, but these do not greatly affect the explosive properties of the nitroglycerine. They raise the specific gravity somewhat, and may therefore cause a glycerine containing a little water to have the correct specific gravity. Glycerine obtained by fermentation contains traces of trimethylene glycol. This gives a dinitrate which is stated to be as stable as nitroglycerine. Albuminous matter is tested for by lead acetate.

The nitrogen content should not exceed 0.3 per cent. Other tests include sulphides, sulphates, sulphites, thiosulphates, chlorides and arsenic. An important test is the *behaviour on nitration*. A mixture of 1 part by weight nitric acid (sp. gr. 1.50) and 2 parts sulphuric acid (sp. gr. 1.84) is placed in a beaker, which is held in the hand in a pail of cold water and kept continuously in motion. Mixed acid from the factory

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may also be used. The temperature is maintained at 12° to 15° and the glycerine is allowed to flow in slowly. One part of glycerine to eight parts of mixed acid are suitable proportions to employ. Overheating is dangerous and the temperature must not be allowed to exceed 30°. When all the glycerine has been added, the mixture is cooled to 15° and brought into a separating funnel. It is important to observe the readiness with which the nitroglycerine separates from the acids. The separation should take place in ten minutes and should be clean and sharp without flockiness. The acid is carefully run off, and the nitroglycerine is washed repeatedly with water at 40° to 50°, then with lukewarm 2 per cent. sodium carbonate solution,

and again with cold water, and measured in a burette. The yield is calculated from the specific gravity of nitroglycerine (1.60). A pailful of water should be held in readiness, in case it is necessary to drown the charge, by reason of the reaction becoming too vigorous. More accurate estimations are obtained by the use of special apparatus in which the nitration is carried out in a separating funnel cooled externally by water or by a freezing mixture. The stirring is effected by compressed air.

The theoretical yield is 246.7 per cent. of the weight of the glycerine. Naoum gives yields of 225 to 229 per cent.

Glycerol may be detected qualitatively in small quantities by colour reactions dependent on the formation of dihydroxyacetone.

(b) Diglycerine

(CH₂OH CHOH CH₂)₂O. Mol. wt., 166.0; sp. gr., 1.33; B.P., 245° to 250° C. (8 mm.); miscible with water; insoluble in ether.

On heating with small quantities of alkali to 250°-260° glycerine undergoes partial condensation to diglycerine which can be nitrated to diglycerine tetranitrate. This is one of the admixtures which are used to lower the freezing point of nitroglycerine. If the condensation has been carried out with glycerine of good quality, special testing may be confined to the specific gravity (approximately 1.286 at 15° for a content of 30 to 40 per cent. diglycerine). The nitration product gives a nitrogen content of 17.6 to 17.7 per cent. The trial nitration is carried out as described under glycerine. The tetranitrate forms emulsions somewhat readily on washing with water, and it is better to use sodium chloride solution. The tetranitrate retains moisture rather firmly and is more difficult to dry than nitroglycerine.

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(c) Monochlorhydrin

CH₂Cl CHOH . CH₂OH. Mol. wt., 110.5; sp. gr., 1.338; B.P., 213°; miscible with water, alcohol and ether.

Monochlorhydrin consists mainly of α-chlorodihydroxypropane, but contains a small proportion of the β-isomer. Usually a mixture of monochlorhydrin and glycerine is obtained, together with some dichlorhydrin. Small proportions of diglycerine may also be present. Assuming that the monochlorhydrin has been prepared from glycerine of satisfactory purity, it is usually sufficient to ascertain the chlorine content and to ensure freedom from water, hydrochloric acid, and dichlorhydrin. Exact analysis of such a mixture is hardly practicable, but a trial nitration should be included, with a nitrogen determination of the product.

For the determination of chlorine, the mixture is first heated to 115° at 30 mm. pressure. This removes any water and dichlorhydrin. About 5 g. is weighed out and boiled for fifteen minutes with 10 c.c. of a 15 per cent. solution of sodium hydroxide in alcohol. The alcohol is evaporated off and a little water is added. This is boiled for a few minutes and the liquid is acidified with nitric acid and the chlorine determined. The value is somewhat too high owing to the presence of small quantities of dichlorhydrin.

(d) Ethylene Glycol

CH₂OH CH₂OH. Mol. wt., 62.0; sp. gr., 1.116 (15°); M.P., -11.5°; B.P., 194°; miscible with water and alcohol.

Ethylene glycol yields on nitration a dinitrate which is used in conjunction with nitroglycerine to lower the freezing point. It is a colourless liquid which is less viscous than glycerine. It resembles glycerine in its hygroscopicity.

It should contain 97 per cent. of ethylene glycol corresponding to a sp. gr. of 1.1074 (20°/4°) if water is the only impurity. The estimation of glycol can be carried out by the dichromate method as for glycerine. It should be free from mineral matter. The moisture content cannot readily be determined by direct heating on account of the greater volatility of ethylene glycol as compared with glycerine. Somewhat more accurate results may be obtained by distilling off a

portion of the glycol until pure glycol passes over, then interrupting the distillation and determining the moisture approximately in the distillate by drying in a flat dish over phosphorus pentoxide with daily weighings until the rate of loss is constant. A correction must be applied for the ultimate constant loss.

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A trial nitration is carried out as for nitroglycerine. The yield of nitrate may be depressed slightly by the presence of small quantities of higher homologues.

(e) Pentaerythritol

$C(CH_2OH)_4$. Mol. wt., 136.0; M.P., 253°; soluble in 100 parts water, 5.5 at 15°.

Pentaerythritol is used for the manufacture of the tetranitrate (Penthril) which is a powerful explosive. It is a white or slightly yellowish crystalline compound. The melting point should be at least 220° to 230° and the compound should be completely soluble in water. According to Pushin, pentaerythritol undergoes allomorphic transformation at 185° and melts at 256°.

IX. AROMATIC HYDROCARBONS AND DERIVATIVES

(a) Hydrocarbons

Benzene and toluene are used for the manufacture of nitro-compounds; xylene is used to a minor extent. They are colourless liquids and should be completely neutral. They are insoluble in water, but mix with most organic solvents.

	Benzene	Toluene	Xylene
Melting point	5.2°	-94°	...
Boiling point	80.4°	110.3°	136° to 140°
Sp. gr. (20° C.)	0.879	0.866	0.868

In the distillation of benzene and toluene 90 per cent. should pass over within a range of 0.6°. For the distillation, 100 c.c. are placed in a distillation flask of about 200 c.c. capacity. This rests on a sheet of asbestos with a hole of 1 in. diameter in the centre. The flask is surrounded by an aluminium cylinder which reaches nearly to the level of the side tube. Xylene is a mixture of isomers of somewhat indeterminate boiling point.

Small percentages of *aliphatic hydrocarbons* are usually present. These should be as low as possible, as they do not undergo nitration. The specific gravity gives some indication of their presence, but a trial nitration is more certain. The hydrocarbon is nitrated to the mono-nitro-compound by a mixture of concentrated sulphuric acid and nitric acid (sp. gr. 1.42) at about 10° with vigorous stirring. The mixed acid is added very slowly to the hydrocarbon and the stirring is continued for an hour after all the acid has been added. The acid is drawn off, and the nitro-compound washed with water with addition of soda to render it alkaline. The separated oil is steam distilled until the drops sink in water. The water is separated and the oil is treated

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again with nitration acid in a graduated cylinder. The unnitratable hydrocarbons form the top layer.

An alternative method is by sulphonation. Evans describes the following method for toluene. A measured quantity (about 50 c.c.) of toluene is added to 150 c.c. of 98 per cent. sulphuric acid in a 250 c.c. graduated cylinder. The cylinder is carefully shaken, so that the temperature does not exceed 45° and the stopper is lifted frequently to avoid excess pressure. The cylinder is allowed to stand for five minutes and vigorously shaken for three to four minutes. The liquid is transferred to a separating funnel, the neck of which is narrow and graduated in 1/100 c.c. The bottom outlet of the funnel is connected by a rubber tube with a mercury reservoir. By this means the acid can be raised until the paraffin layer is contained in the narrow neck. The volume is read after two to three hours. A correction for solubility of 0.6 of the percentage of paraffins found is allowed.

Thiophene is detected by shaking in the cold with a sulphuric acid solution of isatin. This gives a blue coloration in presence of

thiophene. This may be used as a colorimetric method for the estimation of thiophene.

Naphthalene is also used for the manufacture of nitro-derivatives. It should be in the form of pure white crystals of melting point 79° or over. It should not become yellow on exposure to air and light. It should give no residue on sublimation. A solution in concentrated sulphuric acid should give only a faint red colour. On boiling with water it should give no acidity. It should dissolve completely in benzene to a colourless clear solution. Naphthalene forms a sparingly soluble picric acid compound, which can be made use of in its estimation.

(b) Phenol

C_6H_5OH . Mol. wt., 94; sp. gr., 1.066 (15°); M.P., 41°; B.P., 181.5°; soluble in 100 parts water at 15°, 10.3; completely miscible at 84°.

Pure phenol forms colourless crystals; the commercial product has as a rule a slight reddish colour. A setting point of 40° is usually specified; a lower setting point indicates the presence either of water or of cresols. It should give a clear solution in 10 per cent. sodium hydroxide solution.

Phenol is used for the manufacture of picric acid. Metacresol can be similarly converted to trinitrometacresol. Technical metacresol contains ortho- and paracresol. On nitration these isomers are oxidised to oxalic acid. An approximate estimate of the content of metacresol can be obtained by a trial nitration under definite

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conditions. The pure metacresol gives 174 per cent. by weight of trinitro-compound, and the yield is proportional to the meta-content in mixtures of the isomers.

(c) Dimethylaniline

$C_6H_5N(CH_3)_2$. Mol. wt., 121.0; sp. gr., 0.955; M.P., 2°; B.P., 193°; slightly soluble in water; soluble in organic solvents.

Dimethylaniline serves for the preparation of tetryl (trinitrophenyl methyl nitramine). It may contain water, aniline and monomethylaniline. It should be light in colour, free from mineral matter, and should give a clear solution when mixed with an equal volume of concentrated hydrochloric acid.

The presence of aniline is shown by the carbylamine reaction. Aniline and monomethylaniline react with acetic anhydride. An approximate estimate can be obtained by the rise of temperature when 50 c.c. of the dimethylaniline and 10 c.c. of acetic anhydride are brought together in a Dewar vessel. A comparative experiment should be made with dimethylaniline containing a known amount of monomethylaniline. Alternatively the amount of acetic anhydride used up may be determined by filtration. A weighed quantity of acetic anhydride (about 2.5 g.) is added to a weighed quantity of dimethylaniline (about 10 g.). The acetylation is allowed to proceed for two to three hours, 70 c.c. of water added and the whole warmed on a water-bath for half an hour and then titrated with sodium hydroxide. This gives the quantity of acetic anhydride not used in acetylation.

X. SOLVENTS

(a) Acetone

CH_3COCH_3 . Mol. wt., 58.0; sp. gr., 0.7912 (20°/4°); B.P., 56.1°; soluble in water and organic solvents. For acetone and water density tables see Reilly and Ralph.¹

Acetone should be colourless and completely miscible with water. Its specific gravity should not exceed 0.800 at 15°. It should give no turbidity on mixing with twenty times its volume of carbon disulphide, and no residue on evaporation. It should be free from acidity, except for traces of dissolved carbon dioxide (approximately 0.01 per cent.). To test acidity the acetone is boiled to remove carbon dioxide, diluted with an equal volume of water (free from carbon dioxide) and titrated with alkali, using phenol phthalein as indicator. Alkalinity should be absent, as it indicates the presence of amines; it is tested for by diluting

and adding methyl red or para-nitrophenol.

Alcoholic impurities are detected by means of a reagent made

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up by dissolving 0.5 g. of potassium dichromate in 100 c.c. of nitric acid (sp. gr. 1.332). One c.c. of the acetone is mixed with 3 c.c. of the reagent, and allowed to stand for five minutes. No blue or violet colour should be formed.

Aldehydes and similar reducing substances are tested for by the permanganate test. A solution of 1 g. potassium permanganate in a litre of water is made up and 1 c.c. of this is added to 100 c.c. of acetone. The colour should persist for at least thirty minutes at 15.5° in the dark. In Germany, a silver nitrate test is included to detect aldehydes: these can also be detected by Schiff's reagent (fuchsin-bisulphite). "Light oils" also reduce ammoniacal silver nitrate. They may be tested for as follows.

Method 1. 100 c.c. acetone and 200 c.c. water are mixed and rapidly distilled in a retort. The first 10 c.c. of distillate is collected in a graduated cylinder, 20 c.c. of water added, and the volume of any oil which separates on standing is measured.

Method 2. 10 c.c. of acetone is added to 100 c.c. of water at 15°. Two c.c. of a solution containing 12.69 g. iodine and 14.60 g. potassium iodide is added. After exactly one minute, 2 c.c. of *N*/10 thiosulphate is added and the excess of thiosulphate titrated with iodine. One c.c. of *N*/100 iodine solution is equivalent to approximately 0.02 per cent. of the impurity.

The acetone content is usually estimated by Messinger's method. Two g. of acetone is mixed with 500 c.c. water; 10 c.c. of the mixture is mixed with 25 c.c. *N*/1 alkali and 50 c.c. *N*/10 iodine added with shaking. The mixture is shaken frequently and after fifteen to twenty minutes 26 c.c. of *N*/1 sulphuric acid added. The iodine is titrated with thiosulphate. The acetone is converted to iodoform; six atoms of iodine correspond to one mol. of acetone.

A method depending upon the action of mercuric sulphate is also stated to give satisfactory results.

Acetone may be detected qualitatively either by the above reactions or by the following test: The liquid is diluted with water, 2 drops of 5 per cent. nitroprusside, 2 drops of 5 per cent. sodium hydroxide and 5 or 6 drops of acetic acid are added. Acetone gives a red colour changing to violet on warming.

(b) Ethyl Ether

(C_2H_5O). Mol. wt., 74.0; sp. gr., 0.713/15°; B.P., 34°; partially soluble in water; miscible with most organic solvents.

The liquid should be clear and colourless. The specific gravity is usually prescribed (e.g. 0.722) at 15°. The boiling point should be

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between 34° and 36°. The residue on evaporation should not exceed 0.002 per cent. On shaking with water, the aqueous extract should not be acid to litmus. In some specifications the acid is limited to 0.006 per cent. (as CH_3COOH).

Water may be tested for by anhydrous copper sulphate or by aluminium ethylate. Alcohol may be detected by the iodoform reaction, but acetaldehyde also gives this reaction. Acetaldehyde gives a greyish precipitate of mercury with Nessler's reagent.

In Germany, a test which is used for acetaldehyde and vinyl alcohol is to add 5 g. solid potassium hydroxide to 30 c.c. of ether and allow to stand in the dark with shaking. After an hour there should be no separation of yellow or brown solid.

Hydrogen peroxide and organic peroxides may be detected by potassium iodide. Middleton gives the following method: 130 c.c. of 2.5 per cent. sulphuric acid is boiled, carbon dioxide being bubbled through the liquid. Five g. of ferrous sulphate is dissolved in it, and after cooling to 40°, 30 c.c. of a 10 per cent. solution of potassium thiocyanate added, and then, drop by drop, a *N*/300 solution of titanous chloride until the brown colour disappears. Five c.c. of this reagent is put into a 35 c.c. flask which is then filled with ether to the

neck and allowed to stand for five minutes with occasional shaking. Peroxides are indicated by a brown colour, and may be determined by titration with *N*/300 titanous chloride.

Sulphur compounds are tested for by shaking with mercury. One drop of mercury should give no discoloration when shaken in presence of air with 10 c.c. of ether which has been acidified with a few drops of acetic acid.

(c) Ethyl Alcohol

C_2H_5OH . Mol. wt., 46.0; sp. gr., 0.789 at 20°; B.P., 78.3°; miscible with water and with most organic solvents with which it forms azeotropic mixtures.

The liquid should be clear and should give no turbidity with water. It should give no smell of fusel oil, and practically no residue on evaporation (0.01 per cent.). It should be as free as possible from acidity.

Fusel oil may be detected by adding water, shaking out with chloroform, separating, and allowing the chloroform to evaporate. The residue with addition of dilute sulphuric acid should give no smell of fusel oil. Fusel oil may be estimated quantitatively by oxidation to valeric acid.

Acetaldehyde and other aldehydes are tested for by ammoniacal silver nitrate; this should not become coloured or turbid on standing for a short time. Nessler's reagent should give only a slight precipitate.

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Schiff's reagent may also be used. Siebert recommends a method in which the aldehyde is converted to aldoxime by hydroxylamine hydrochloride. Acid is liberated in the reaction, and is titrated with sodium hydroxide.

Acetone gives a red colour with sodium nitroprusside and alkali: aldehyde reacts similarly. More distinctive is the vanillin reaction; 2 c.c. of a solution of 15 g. vanillin in 100 c.c. alcohol is mixed with 3 c.c. of the liquid under test and 1 c.c. conc. sulphuric acid. Acetone gives a carmine red colour, which turns yellow on addition of water. Alkali turns the colour bright orange red.

Methyl alcohol may be detected and estimated by conversion to methylaniline by means of iodine, phosphorus and aniline, followed by oxidation by stannic chloride to methyl violet. Other methods depend upon the conversion of the methyl alcohol to formaldehyde, which gives various colour reactions, e.g. with morphine sulphate and with fuchsin bisulphite.

Benzene may be separated by shaking with a concentrated solution of calcium chloride. For small quantities the alcohol is diluted with water, a small proportion is distilled over and the distillate shaken with potassium dichromate and hydrochloric acid. After fifteen minutes the solution is shaken with petroleum ether and the increase in volume of the petroleum ether layer is measured.

Ethyl alcohol may be identified in mixtures by conversion to ethyl benzoate or ethyl-*p*-nitrobenzoate by the Schotten-Baumann reaction.

B. ANALYSIS OF EXPLOSIVES

I. BLACK POWDER

Black powder consists of a mixture of nitre, charcoal and sulphur. The proportions vary somewhat, the nitre being generally about 74 to 78 per cent., the charcoal 12 to 16 per cent., and the sulphur 9 to 12 per cent. Allied mixtures are met with containing sodium nitrate in place of potassium nitrate, coal or soot in place of charcoal and occasionally other ingredients, such as resin, pitch, cellulose, etc.

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(a) General Examination

The powder should show no differences in colour even when pulverised between the fingers. The grains should be hard, and on grinding the powder should break first into sharp-edged fragments. When poured over a sheet of white paper it should not leave traces of black dust. The size of grain is measured by sieving. The apparent

density is found by pouring the powder into a measuring vessel, striking off the excess with a straight-edge, and weighing.

The "absolute" density is measured by displacement of mercury. An apparatus for this purpose was devised by Bianchi. In this method the air is removed from the interstices by evacuation. In the method used by the U.S.A. Bureau of Mines a vacuum pump is not required. These methods give figures of 1.65 to 1.85. This is not, however, the true absolute value, as the mercury does not penetrate into the finer interstices.

Gun-powder tends to absorb moisture in a damp atmosphere. The hygroscopicity may be determined by placing a weighed quantity on a small tray with a bottom of fine wire gauze enclosed in a box containing a saturated solution of potassium nitrate. The powder is left in the box for one to two days, according to the size of the grains, and is then weighed. Alternatively the gun-powder may be placed in a saturated atmosphere in comparison with a standard sample.

After storage in a damp atmosphere efflorescence of potassium nitrate crystals may occur. This can be detected under the microscope. Except for such efflorescence there is no tendency for the ingredients to segregate. If stored in contact with metals some reduction of the nitrate to nitrite may occur.

(b) Chemical Examination

Moisture. As sulphur is slightly volatile at 100° the moisture is estimated by heating at 70° for one and a half to three hours, or by drying in a desiccator over sulphuric acid for three days. Limits range from about 0.8 to 1.2 per cent.

Acidity. When the powder is extracted with water, the solution should not be more than very faintly acid to litmus paper.

Potassium Nitrate. Ten g. of the powder is extracted with warm water in a Gooch crucible, about 200 c.c. of water being added in quantities of 15 to 20 c.c. at a time. The final washings should give

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no residue on evaporation. The diphenylamine test may also be used to see if the extraction is complete. The loss of weight of the crucible and contents, after drying at 70°, gives the percentage of potassium nitrate after allowing for the moisture content. As the charcoal contains a little water-soluble matter, it is necessary, for accurate determinations, to evaporate an aliquot portion of the filtrate and to heat it to incipient fusion. An estimate of the nitrate by means of the nitrometer is occasionally included.

The nitrate may be tested for chloride, sulphate, perchlorate, etc. (see Potassium Nitrate, p. 1).

The dried material in the crucible is extracted with carbon disulphide which has been recently distilled, until the washings give no residue of sulphur. The residue is dried in a warm place (avoiding flames) and finally at 100°. The loss of weight gives the sulphur.

In Gay-Lussac's method, 5 g. of the fine powder is mixed with 5 g. dry sodium carbonate. Five g. pure potassium nitrate and 30 g. sodium chlorate are added and the whole well mixed in a mortar, and ignited in a platinum crucible. After cooling, the mixture is dissolved in water, oxidised with bromine solution, acidified, and the sulphate estimated as barium sulphate.

Another method is to oxidise the original powder with 11 parts of pure conc. nitric acid and 2 parts of potassium chlorate until the liquid is clear and yellowish. The nitric acid is evaporated and the sulphur determined as sulphate. Petersen boils the powder with sodium hydroxide and hydrogen peroxide, and estimates as sulphate. Oehman gives a method in which the water-insoluble material is burnt in a bomb calorimeter.

Charcoal. This forms the residue after extraction of the potassium nitrate and sulphur. It should be examined for ash and total carbon content. It is also examined microscopically for wood meal, soot, etc.

It is sometimes preferred to proceed as follows: after the moisture estimation, a separate sample of 2.5 g. of the powder is extracted with

carbon disulphide and the insoluble part weighed. From this the sulphur is calculated. For the nitrate, 2.5 g. is shaken with 250 c.c. of water and left overnight. An aliquot part is then evaporated to dryness and weighed. If desired, the nitrate may be converted to sulphate by adding sulphuric acid, drying and igniting; this removes organic matter. The charcoal is determined by difference.

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II. NITRIC ESTERS

(a) Nitrocellulose

Nitrocellulose, as prepared from cellulose by nitric and sulphuric acids, consists of small fibres similar to the original cellulose. A microscopic examination gives an indication of the nature of the cellulose used for nitration. The length of fibre shows whether the pulping has been efficient. Apart from its rapidity of burning nitrocellulose may be distinguished from cellulose by acetone or ethyl acetate. These solvents gelatinise nitrocellulose, but do not affect cellulose. It may also be tested for nitrogen by diphenylamine and sulphuric acid. Some information as to the degree of nitration may be obtained by examination under polarised light.

Ungelatinised nitrocellulose will usually be received in the wet condition. The moisture can be determined, if required, by mixing the sample thoroughly, rubbing through a metal sieve, weighing out about 10 g. rapidly, and drying in a steam oven. Sometimes a lower temperature (50°) or evacuation over sulphuric acid is prescribed. If the stability of the dried nitrocellulose is to be determined, calcium chloride should be used as drying agent.

For the chemical tests, the sample is prepared by squeezing out the moisture as far as possible between layers of pure filter paper, teasing out loosely, drying at 50° and transferring to a desiccator.

Mineral Matter. About 3 g. of the nitrocellulose is weighed into a tared silica dish, covered with a layer of molten paraffin wax, stirred and ignited, care being taken to avoid loss. After all has burnt off, the contents of the dish are moistened with ammonium carbonate, dried and treated to 105-110°. Sometimes sulphuric acid is used for moistening, and the residue ignited. Another method is to moisten the nitrocellulose with nitric acid and heat on the water-bath. The residue is then ignited. After cooling, a little water is added, evaporated, and the residue again ignited.

Calcium Carbonate. Ten g. of nitrocellulose, 100 c.c. of *N*/10 hydrochloric acid and 100 c.c. water are put into a stoppered cylinder, shaken for an hour, and the excess of acid titrated with *N*/10 sodium carbonate, using methyl orange as indicator.

Soluble Salts. Nitrates are sometimes mixed with nitrocellulose and may be determined by extraction with water.

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Paraffin Wax. A coating of wax is sometimes present; this can be extracted with ether.

Stability Tests. The tests are described in Section C (p. 70 *et seq.*). The Heat test, Bergmann and Junk test, and Will test are frequently applied. A limit of 10 mins. at 170° F. is laid down by the Home Office for the Heat test.

Nitrogen. Numerous methods have been applied to this determination.

They include gravimetric methods (nitron), volumetric methods depending on reduction of the nitric acid to ammonia, and gas volumetric methods. The methods most commonly used are the nitrometer method (Lunge) and modifications of the Schulze-Tiemann method, depending on the action of ferrous chloride.

Nitrometer method.

The nitrocellulose is passed through a sieve and dried. About 0.6 g. is weighed into a small weighing bottle. To ensure complete drying the bottle and contents may be dried for an hour in a steam oven and weighed. Concentrated sulphuric acid (6 to 8 c.c.) is added and allowed to stand for twenty to thirty minutes to dissolve the nitrocellulose. The solution is washed with small quantities of sulphuric

acid into the cup of the nitrometer and allowed to flow into the bulb. This should be done without delay. About 0.5 c.c. water is added to the last portion of sulphuric acid. The nitrometer is shaken and the nitric oxide is measured in the usual way. The shaking should not be too prolonged, as this decreases the gas volume. The nitric oxide contains traces of other gases (carbon monoxide, etc.) which tend to increase the gas volume; on the other hand a little nitric oxide is absorbed by the sulphuric acid. The solubility is at a minimum in 85 per cent. sulphuric acid. Webb and Taylor recommend the use of 91 to 92 per cent. sulphuric acid, and allow 0.2 c.c. in 10 c.c. acid for the solubility.

In the Du Pont nitrometer direct readings of the nitrogen percentage can be made without the necessity of correcting the volume of gas to standard temperature and pressure. The apparatus consists of (1) a generating bulb with mercury reservoir attached, as in Lunge's nitrometer, and (2) a reading apparatus, with a closed compensator

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bulb containing dry air. The generating bulb has a two-way stop-cock, connecting either with the cup or with an exit tube. The sample is introduced and shaken with mercury and sulphuric acid. The quantity must be such that the gas volume is between 171.8 and 240.4 c.c. The nitric oxide is transferred to a reading burette, which is connected at its lower end by rubber tubing to (1) a mercury reservoir and (2) a closed compensator bulb with a lower tube which is marked with a graduation mark. The levels are adjusted so that the mercury is at the level of the graduation mark on the compensator tube, and is at the same time balanced between this and the reading burette. The reading is then taken. The reading burette is calibrated from 10 to 14 per cent. of nitrogen for 1 g. of substance. The instrument is standardised by carrying out a measurement with pure potassium nitrate.

The Schulze-Tiemann method depends upon the action of boiling ferrous chloride solution in presence of hydrochloric acid. This converts the nitrogen of the nitrocellulose to nitric oxide.

The apparatus used in Reinhold's method is shown in Fig. 1. The vessel in which the gas is evolved consists of a round-bottomed flask of 300 c.c. capacity made of Jena glass with a long neck. The stopper is of glass and is connected with two glass tubes as shown. The connection between stopper and flask is made by means of a short length of rubber tube which is fitted between the two and makes a gas-tight joint.

The tube A is connected by a rubber tube with a glass tube about 12 cm. long, constricted at the end, and dipping into a small beaker of water. The tube B is connected by a rubber tube with a forked glass tube. One of the branches is connected to a drawn-out tube dipping into water. The other is joined by a short rubber tube to the measuring apparatus. Spring clips are affixed to the rubber joints as shown.

The flask is clamped over a bunsen burner with a small flame. The measuring apparatus consists of the measuring tube (M), the levelling tube (N), and a connecting tube (Z) of special construction,

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which enables the flask in which the gas is evolved to be connected with the measuring tube. The upper portion of the measuring tube is widened, and the calibrations commence at 100 c.c. at the place where the tube narrows, and extend to 130 or 150 c.c. The tube is jacketed as shown, to permit of cooling by water. The levelling tube is of the same internal diameter as the measuring tube, and is also jacketed. The tube with pinch-cock at the bottom serves to draw off the liquid

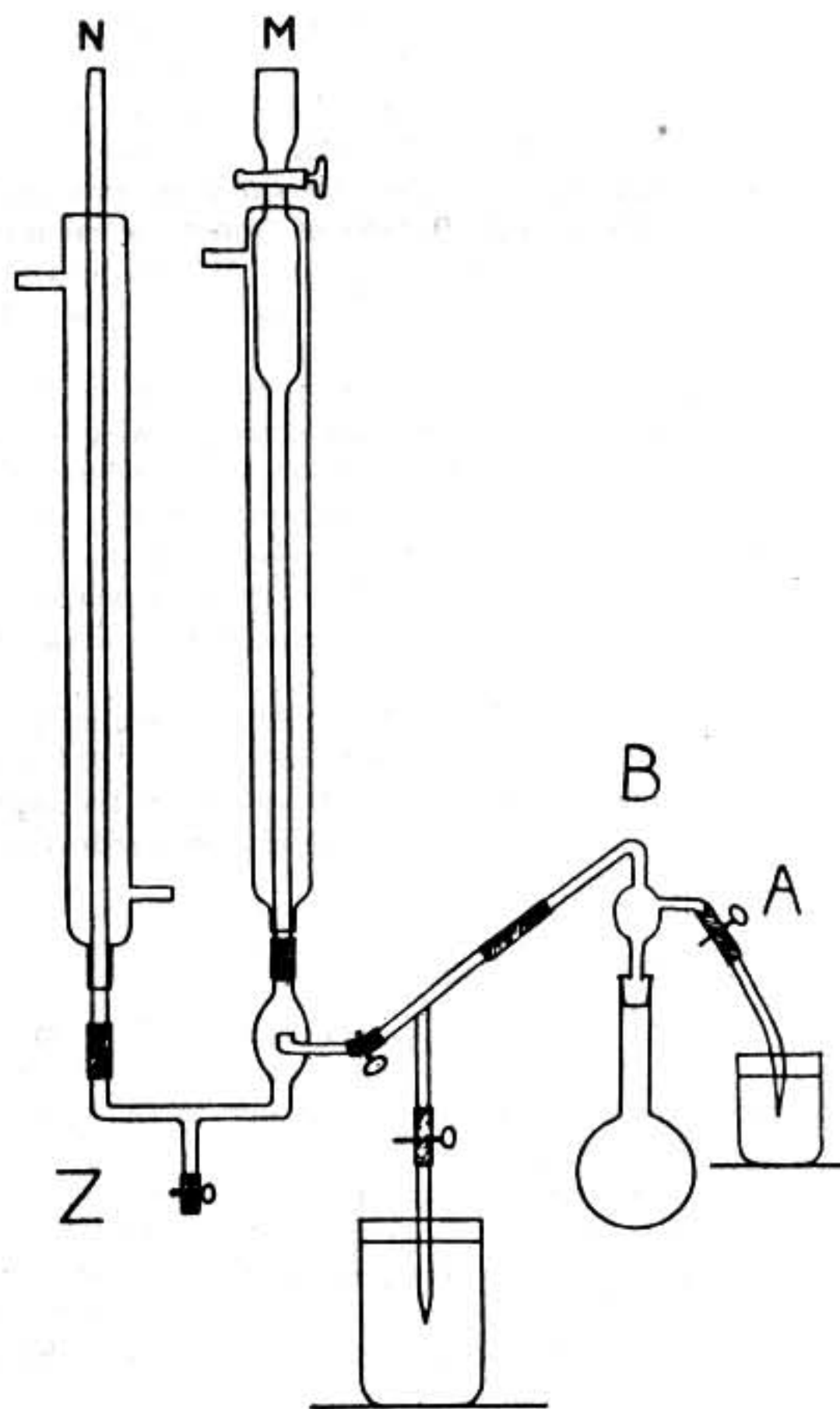


FIG. 1.

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as required. The liquid consists of 30 per cent. potassium hydroxide. The measuring tube and levelling tube are filled and the tube leading to the flask is filled as far as the junction of the two tubes.

The nitrocellulose is dried and 0.6 g. weighed into the flask, 30 c.c. of water being then added. The apparatus is connected up as shown. The flask is heated over a free flame, the clips remaining open. When all the air has been expelled, both clips are closed and the flame is simultaneously removed; 25 c.c. of concentrated ferrous chloride is put into the smaller beaker and sucked into the flask by opening the clip cautiously to avoid influx of air. Thereupon 20 c.c. conc. hydrochloric acid is introduced in the same way, and finally a small quantity of water. The flask is then heated carefully until the rubber connections show signs of a positive pressure, and on cautious opening of the pinch-cock no more liquid enters the flask. The pinch-cock connecting the flask with the measuring tube is opened, and the nitric oxide is driven over, the contents of the flask being vigorously boiled. At the same time the cooling water is set in action, and a thermometer suspended in the cooling-jacket. When no more gas passes over, the pinch-cock is closed, the flame is removed, and the flask allowed to cool somewhat. This sets free the dissolved nitric oxide, and the flask is again heated to drive over the remaining nitric oxide. When the gas evolution comes to an end, the pinch-cock is closed, and the flame is turned out, and the alkaline liquid is drawn off from the cock at the bottom of the measuring tube and levelling tube, until the liquids are at the same level in both tubes. The volume of gas can be read off at once. The temperature and barometric pressure are also read. The two tubes should be at approximately the same temperature. The nitrogen content is readily calculated from the volume of nitric oxide.

The ferrous chloride solution is made by warming conc. hydrochloric acid with excess of iron nails, filtering, and adding a little

conc. hydrochloric acid. It should be moderately fresh. All solutions must be free from dissolved air.

The Schulze-Tiemann method is generally found to give somewhat low results, compared with the nitrometer.

For the determination by the nitron method 0.2 of nitrocellulose is brought into a 150 c.c. Erlenmeyer flask with 5 c.c. of 30 per cent. sodium hydroxide solution and 10 c.c. of 3 per cent. hydrogen peroxide, warmed for a few minutes on the water-bath until frothing ceases, and then boiled on a free flame. The nitrocellulose should pass into solution in a few minutes. After cooling, 40 c.c. of water and 10 c.c. of hydrogen peroxide solution are added, the solution warmed to 50° and 40 c.c. of 5 per cent. sulphuric acid allowed to flow into the

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bottom of the flask by a pipette. The solution is further warmed to 80° and 12 c.c. of nitron acetate added (10 per cent. solution of nitron in 5 per cent. acetic acid). After cooling and standing for one and a half to two hours (preferably at 0°) the nitron nitrate is filtered off and washed three or four times with 10 c.c. of ice-cold water. The precipitate is dried at 110°. From the weight of the $C_{20}H_{16}N_4HNO_3$ (mol. wt. 375) the nitrogen content of the nitrocellulose is calculated.

Unnitrated Cellulose. Five g. of nitrocellulose is boiled for half an hour with a saturated solution of sodium sulphide, allowed to stand for twenty-four hours, the solution decanted, and the residue boiled again with fresh sodium sulphide. The insoluble matter is collected on a linen filter of known weight, washed with hot distilled water until free from sulphide, then with dilute hydrochloric acid and finally with water until free from chloride. The residue is dried at 50° and weighed. It is then ignited in a platinum crucible and the weight of the ash deducted from that of the total residue.

According to Lunge and Weintraub the sodium sulphide method is inaccurate, as the residue contains nitrocellulose. They therefore worked out a method in which the nitrocellulose is treated with sodium ethylate and acetone.

Another method is to boil 5 g. nitrocellulose for forty minutes with 30 c.c. of a solution of stannous chloride in excess of sodium hydroxide, allow to stand for twenty-four hours, decant carefully, boil the residue again with 30 c.c. of the solution, filter, wash with water, then with 5 per cent. hydrochloric acid and again with water, dry and weigh. Then ignite and deduct the weight of the ash.

The unnitrated cellulose may also be determined by dissolving the nitrocellulose in acetone. Five g. of nitrocellulose is treated with a litre of acetone and allowed to stand for twenty-four hours with frequent shaking. The solution is decanted, the residue filtered, washed with acetone, dried at about 70°, and weighed.

Solubility in Ether-Alcohol. The lower nitrates of cellulose are in general more readily soluble in a mixture of ether and alcohol than the higher nitrates. The general method of testing is to introduce a weighed quantity of nitrocellulose into a measuring cylinder and shake with a mixture of ether and alcohol. The temperature at which this is done is of importance; sometimes 15.5° is specified, and sometimes 20°. After shaking at frequent intervals for six hours, the cylinder is allowed to stand overnight to allow the insoluble nitrocellulose to settle, and an aliquot portion of the clear liquid is withdrawn and evaporated. Usually the bulk of the liquid is distilled off in a flask on a water-bath, and the remainder is washed into a glass dish with ether-alcohol and evaporated to dryness. It is advisable

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to add a little water before or during the evaporation, as this causes the nitrocellulose to separate out in a looser condition in which it can be more readily dried. The temperature is finally raised to 80° and the dish is then cooled in a desiccator and weighed.

The quantity of nitrocellulose and the proportions of ether and alcohol vary somewhat, e.g. 2 to 4 g. may be treated with 150 c.c. of ether-alcohol (2:1). In Germany the proportion of ether to alcohol is 4:3, 2 g. of nitrocellulose being shaken with 215 c.c. alcohol and 285 c.c. ether. In some cases it is preferred to shake first with alcohol and then add the required quantity of ether, as this avoids the formation

of gelatinous lumps.

The above method is in general use for gun-cotton, which is mainly insoluble in ether-alcohol. It may also be used for nitrocelluloses which are almost completely soluble, but alternative methods have been devised for the latter in which the insoluble portion is estimated. Thus, after treatment with ether-alcohol and settling, the clear liquid may be siphoned off and the residue again treated with ether-alcohol, the treatment being repeated as required. The residual suspension is ultimately filtered through a filtering tube fitted with a plug of asbestos, and the insoluble matter dried and weighed. A shortened method is also described in which the liquid, after standing, is transferred to a tube which is tapered at the bottom to a narrow graduated portion. An approximate estimate of the insoluble nitrocellulose may be obtained from the volume which it occupies in the narrow part of the tube.

Sulphates. These include sulphuric esters together with any inorganic sulphate ($CaSO_4$). Dunclicliff gives the following method: 5 g. of nitrocellulose is heated on a water-bath with 50 c.c. conc. nitric acid until the nitrocellulose has dissolved and brown fumes have ceased. About 1 g. sodium chlorate is added in small quantities and the whole evaporated to dryness. The residue is treated with 20 c.c. of hydrochloric acid and 0.5 sodium chlorate (added in small quantities) and the liquid again evaporated to dryness. This latter treatment is repeated. This converts all sulphuric esters to soluble sulphate, which may be estimated in the usual way. A blank test is made to allow for sulphate in the reagents.

An alternative method is to destroy the nitrocellulose by boiling with nitric acid containing potassium nitrate, heat the residue strongly, dissolve in hydrochloric acid, filter, and determine the sulphate.

Mercury. Traces of mercury mask the heat test, and it is important to ensure its absence. Probably the most sensitive method for the detection of mercury is to examine the spectrum given by an electrical

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discharge through a vacuum tube containing the material under test, the latter being kept at a temperature of 100°. Alternatively the explosive under test may be heated in a vessel in which gold leaf is placed, and the gold leaf subsequently tested in the vacuum tube. In the latter method the presence of mercury is also shown by whitish-grey spots of amalgam on the gold.

Viscosity. The nitrocellulose is dissolved in ether-alcohol or acetone and the viscosity determined in a viscometer. It is usual to find the time required by a steel ball to drop through a measured height of the solution.

For the detection of nitrocellulose in explosives, Stansky recommends extracting with acetone, evaporating the solution to a small bulk and adding chloroform to precipitate the nitrocellulose. This is then hydrolysed with sodium hydroxide solution, and tested for nitrate by diphenylamine and sulphuric acid.

(b) Nitroglycerine

Glyceryl trinitrate, $C_3H_5(NO_3)_3$. Mol. wt., 227.0; sp. gr., 1.600; M.P., 13°; soluble in 100 parts water, 0.14 at 15°, 0.35 at 90°; soluble in organic solvents.

Nitroglycerine seldom comes into commerce as such. The examination of nitroglycerine is therefore as a rule necessary only in works laboratories. If it is in solution in alcohol or acetone, it should be separated by dilution with water and filtered through dry salt.

Nitroglycerine should form a clear, or very slightly turbid, pale yellow liquid. The moisture is estimated by allowing to stand over calcium chloride (not sulphuric acid) in the cold. Nitroglycerine should be practically free from acidity and alkalinity; to test for these, 20 g. is shaken with 50 c.c. of water and the water tested with litmus and if necessary titrated, using methyl orange as indicator.

The nitrogen content is usually determined by the nitrometer method.

Another method is to saponify the nitroglycerine with sodium ethylate and reduce to ammonia with a mixture of powdered zinc and iron.

Stability tests are given under C (p. 70 *et seq.*).

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The limit for the heat test of nitroglycerine extracted from dynamite, etc., is fifteen minutes at 160° F. The nitroglycerine must be dry, as moisture prolongs the test. It should be filtered into the test tube through a dry filter paper, taking care that it does not wet the sides of the tube.

It has been found by Crawford that small quantities of tetranitromethane and nitrochloromethanes are frequently present in nitroglycerine, and depress the heat test. They may be removed by shaking with sodium sulphite solution.

The melting point is occasionally used as a criterion of the purity of nitroglycerine. Nitroglycerine supercools very readily and must be seeded with crystals of the solid substance.

Mixtures of nitroglycerine with tetranitrodiglycerine are tested in general similarly to nitroglycerine. An admixture of 30 per cent. tetranitrodiglycerine lowers the nitrogen percentage to 17.6-17.7. The physical properties of the mixture are not sharply defined; it is a viscous oil of indeterminate freezing point. In its solubilities, etc., it is in general similar to nitroglycerine.

(c) Dinitroglycol

Ethylene glycol dinitrate, $C_2H_4(NO_2)_2$. Mol. wt., 152.0; sp. gr., 1.496 (15°); M.P., -20°; soluble in 100 parts water, 0.6 at 15°; soluble in organic solvents.

Dinitroglycol is a colourless liquid, less viscous than nitroglycerine. It has a very low freezing point and in admixture with nitroglycerine the freezing point is still further depressed. It is a frequent constituent of non-freezing explosives. It dissolves in most organic solvents, but is sparingly soluble in carbon disulphide.

Dinitroglycol is tested similarly to nitroglycerine. It is, however, considerably more volatile than nitroglycerine and loses weight readily on heating, and even to some extent at ordinary temperature. It should give no residue on evaporating at 50° (absence of nitroglycerine, etc.).

The nitrogen content is almost identical with that of nitroglycerine and does not therefore give any indication of the percentage composition of mixtures.

Marqueyrol and Goutal have given methods for the estimation of dinitroglycol in nitroglycerine. These depend on the action of sulphuric acid and the depression of the freezing point of benzene.

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(d) Dinitrochlorhydrin

Chlorohydrin dinitrate, $CH_2ClCH(NO_2)CH_2NO_2$. Mol. wt., 200.5; M.P., α : +5°, β : +16°; sp. gr., 1.541 at 15°; solubility in 100 parts water, 0.23 at 15°; soluble in organic solvents.

Dinitrochlorhydrin forms a colourless liquid with a slightly aromatic odour. The commercial product is yellow to yellowish-brown. It is less viscous and more volatile than nitroglycerine.

Dinitrochlorhydrin always contains a small proportion of nitrodichlorhydrin. A chlorine estimation of a mixture in which nitroglycerine is also present does not therefore give definite evidence of the composition. The nitrogen determination also cannot be relied upon, unless the unchlorinated portion of the raw material is known.

The examination includes determination of specific gravity, nitrogen and chlorine content. The nitrogen content of the pure dinitrochlorhydrin is 13.97 per cent. In practice about 13.80 to 13.85 per cent. is found. The chlorine is estimated by saponification with alcoholic potassium hydroxide (15 per cent.). After boiling for fifteen minutes the liquid is evaporated and the residue heated, then dissolved in water, neutralised with nitric acid, the nitrite oxidised with permanganate, and the chlorine estimated.

In some cases the refractive index is made use of for mixtures, but the results are not usually very reliable.

(e) Starch Nitrate

Nitrated starch is used in the United States as an ingredient of

blasting explosives. The nitration of starch gives nitric esters with about the same nitrogen content as with celluloses. The starch nitrate (often incorrectly designated *nitro-starch*) dissolves readily in acetone and ethyl acetate and to some extent in ether-alcohol. The solutions show a relatively low viscosity. It is much more hygroscopic than cellulose nitrate and is mixed with oils to prevent absorption of water. A partly acetylated starch on nitration gives a less hygroscopic product due to reduction of free hydroxyl groups in the nitrated product.

The nitrogen content is determined by the nitrometer method. Difficulty is experienced, as the starch nitrate does not dissolve very readily in the sulphuric acid. It may, however, be dissolved by shaking in a stoppered bottle and then introduced into the nitrometer.

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Carbonates are estimated as in cellulose nitrate. Stability tests are also included. In America the loss of weight at 100° is measured (see Section C, VI. (a), Sy's method, p. 85). The stability is somewhat poor.

(f) Nitromannite

Mannite hexanitate, $NO_2 \cdot CH_2(CHNO_2)_4CH_2NO_2$. Mol. wt., 452; sp. gr., 1.604; M.P., 112° to 113°; insol. water, slightly sol. cold alcohol, sol. ether and acetone.

This forms a somewhat voluminous white crystalline powder, which should give a clear solution in ether. The pure compound contains 18.58 per cent. of nitrogen and the technical product approaches this value. The stability is somewhat poor and the explosive is expensive. The purity of the compound is best determined by the melting point.

(g) Nitrated Polysaccharides

Recently, in addition to nitrated celluloses, starch nitrate, etc., various nitrated products of other polysaccharides have received attention, e.g. nitrated inulin, nitrated lichenin. The following is an example of the preparation of one of these products on a small scale:

Finely powdered lichenin (1 part) was gradually added at room temperature to a mixture (50 parts) of 3 parts by weight of sulphuric acid (sp. gr. 1.84) and 1 part by weight of nitric acid (sp. gr. 1.5). After each addition of lichenin, the nitration mixture was stirred. The lichenin nitrate was separated by decantation, and purified by boiling for a short time first with slightly acid water, then with alkaline tap water, finally with distilled water, and then dried at low temperature. $C_{12}H_{15}O_8(NO_2)_8$ requires N = 12.7 per cent.

Lichenin pentanitate is readily soluble in acetone, ethyl acetate, and amyl acetate, but insoluble in ether, benzene, and water. When gelatinised with a solvent, it gives a product resembling horn. Like nitrocellulose of the same percentage nitrogen composition, it is almost completely soluble in a mixture of ether and alcohol, and decomposes at high temperatures, giving off oxides of nitrogen.

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(h) Tetranitropentaerythritol (Penthril)

Pentaerythritol-tetranitrate, $C(CH_2NO_2)_4$. Mol. wt., 316.0; sp. gr., 1.73 to 1.74; M.P., 140° to 141°; insol. water, slightly sol. in ether, sol. acetone.

Pentaerythritol-tetranitrate should be in the form of fine white crystals and should have no tendency to agglomerate. The technical product melts at 135° to 137°. The pure compound (M.P. 138.5° to 141°) gives a clear solution in warm acetone, but a slight residue of calcium salts is usually found. The compound should be neutral. The nitrogen content of the pure compound is 17.74 per cent.; usually a percentage of 17.3 to 17.4 is found. Other tests include ash, moisture and acidity. The last is determined by dissolving in acetone, reprecipitating with water, filtering and testing the filtrate for sulphuric and nitric acid.

III. AROMATIC NITRO-COMPOUNDS

A number of higher nitro-compounds of benzene derivatives are used for military purposes, e.g. trinitrotoluene and trinitrophenol. Mono- and dinitro-compounds are used in industrial explosives. The separation of mixtures of nitro-compounds is somewhat difficult; in some cases steam distillation is of assistance, a partial separation may be effected by solvents, and certain colour reactions are used. Several general tests for the nitro-group have been described. Olivier recommends dissolving in benzene and adding aluminium chloride; nitro-compounds give a red colour. Mulliken and Barker dissolve the nitro-compound in alcohol, add a trace of calcium chloride, reduce with zinc and test for the hydroxylamine group by the silver mirror test. In an alternative method, 3 to 4 drops of the compound are boiled with 2 c.c. of a mixture of equal parts of aniline and ortho- and para-toluidine together with 2 c.c. of water, 2 c.c. of conc. hydrochloric acid and a gram of iron filings. This gives fuchsine, which on pouring into dilute acetic acid gives a red colour. A number of the nitro-compounds give characteristic colours with alkalis and these are of assistance in the identification of the compounds.

For the quantitative estimation the nitrometer method is not in general applicable, though the nitramine group in tetryl responds to this test. The Dumas method may be used under precautions, and the Kjeldahl method is sometimes used for the lower nitro-compounds. Titration methods depending on reduction with stannous chloride are described by Limpricht,

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Reduction with titanous chloride and sulphate is also employed.

The tests which are applied to nitro-compounds usually include setting point, volatile matter, free acid, residues insoluble in organic solvents, and ash. Occasionally special tests for exudation, etc., are specified.

(a) Picric Acid

Trinitrophenol ($\text{NO}_2)_3\text{C}_6\text{H}_2\text{OH}$. Mol. wt., 229.0; sp. gr., 1.76; M.P., 121.6°; soluble in 100 parts water, 0.8 at 0°, 6.33 at 100°; soluble in organic solvents.

Picric acid should be of uniform yellow colour and free from visible impurities. It should melt to a yellow or light brown liquid, which should not darken on continued heating. The melt should be practically free from scum or deposit.

Metallic picrates and oxalates should be absent, and other nitro-compounds should be present only in traces. The melting point or setting point carried out on a well-dried sample should be at least 120°. The moisture content is generally limited to 0.1–0.25 per cent., and the ash to 0.05–0.1 per cent.; this should not be of a gritty nature. Impurities insoluble in water should not exceed the ash content by more than 0.05 per cent. The picric acid should be almost completely soluble in benzene. Sulphates are restricted to 0.05–0.1 per cent. (as SO_3). Chlorides and nitrates are sometimes tested for. Absence of lead in any form which might give rise to the formation of lead picrate is of special importance. Lead sulphate is, however, comparatively harmless.

The setting point is determined by allowing the molten acid to cool slowly in a broad air-jacketed test tube.

The volatile matter is measured by heating for two hours at 100°, or three hours at 80°, or in a vacuum desiccator over sulphuric acid for twenty-four hours.

For the determination of the ash, 10 g. of the picric acid is added in very small quantities to a heated crucible. The temperature is then raised to burn off carbon, and the residue is moistened with nitric acid, then with a little sulphuric acid, and again ignited. An alternative method is to moisten the picric acid with concentrated sulphuric acid and heat it gradually.

Sulphates are determined in the ordinary way. Large excess of barium chloride should be avoided.

For the detection of picrates, the picric acid is extracted with

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benzene, and the residue is examined under the microscope and tested by burning. The benzene residue is also examined for oxalates.

Nitrophenolsulphonic acids may be estimated by melting with excess of sodium carbonate, determining the sulphate formed and subtracting the sulphate originally present.

Picric acid may generally be detected by its intense yellow colour and dyeing properties, also by its bitter taste. It may be extracted from its aqueous solution by ether after acidifying strongly with sulphuric acid. On heating with potassium cyanide and sodium hydroxide to 60°–70°, picric acid gives a blood-red colour. Ammonium sulphide also gives a red colour with picric acid. Potassium ferrocyanide gives on warming a bright blue colour and ferricyanide a red colour, both of these changing to reddish-violet. Copper ammonium sulphate gives a greenish-yellow precipitate. Methylene blue gives a violet precipitate. Picric acid forms a sparingly soluble potassium salt, and gives characteristic compounds with naphthalene and phenanthrene. The picrates of cinchonine, berberine, acridine and nitron are almost insoluble and may be used for the quantitative estimation of picric acid. Picric acid may be titrated with alkali, using phenol phthalein or methyl red as indicator.

Ammonium picrate forms yellow crystals which dissolve readily in water. It should be practically free from insoluble matter (0.2 per cent.) and should not give more than 0.2 per cent. of ash.

Trinitrocresol resembles picric acid in general, but melts at 107° and gives a readily soluble potassium salt.

(b) Dinitrotoluene

$\text{CH}_3\text{C}_6\text{H}_3(\text{NO}_2)_2$. Mol. wt., 182; M.P., 70.5°; insol. water, soluble in organic solvents.

A large number of industrial explosives contain dinitrotoluene or trinitrotoluene or mixtures of these. The dinitrotoluene is mainly the 1.2.4 isomer, but contains some of the other isomers. Different grades of purity are met with; a good quality material has a setting point of 66° to 68°. It should not smell of mononitrotoluene. The acidity should not exceed 0.1 per cent. and the compound should melt to a transparent yellow liquid. The volatile matter should not exceed 0.25 per cent., and the residue on ignition should not be greater than 0.05 per cent. On dissolving in benzene, the residue should not exceed 0.10 per cent.

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(c) Trinitrotoluene

$(\text{NO}_2)_3\text{C}_6\text{H}_2\text{CH}_3$. Mol. wt., 227.0; sp. gr., 1.68; M.P., 81°; soluble in 100 parts water, 0.02 at 15°, 0.16 at 100°; soluble in organic solvents.

Trinitrotoluene (also known as TNT, trotyl, trinol, etc.) is used as such and also in admixture with ammonium nitrate, etc., in explosives such as amatol, ammonal, sabulite, donarite, etc. This substance is the most important military high explosive.

The pure compound forms pale yellow crystals. The best indicator of the purity is the setting point. At the present time the commercial product is available in a very high degree of purity. The compound must be dry, as the setting point is depressed by water. About 50 g. of the trinitrotoluene is melted in a dish at 100°; any drops of water are removed by means of a filter paper, and the heating is continued for two hours with stirring. The molten material is poured into a broad test tube fitted with a cork and thermometer. This tube is fitted into a wider tube leaving an air space of about 5 mm., and the double tube is placed in a vessel of about 1 litre capacity. The trinitrotoluene is stirred during cooling, and the maximum temperature after crystallisation has set in is observed. For crude trinitrotoluene a setting point of about 76° is usually required, and for purified trinitrotoluene 80° or sometimes slightly higher. The molten trinitrotoluene should be of a medium brown colour and should not darken on continued heating at 100°. It should be clear and should not deposit any particles of grit.

A benzene solution of the trinitrotoluene should contain only traces of insoluble organic compounds (0.1 to 0.2 per cent.).

For the estimation of the ash, 5 g. of the substance is moistened with 2 c.c. sulphuric acid and burnt off. The residue is moistened with a little nitric acid, then with sulphuric acid and reheated. The ash should not exceed 0.05 per cent.

The volatile matter may be estimated by the "dish and cone" method (see Smokeless Powder, p. 50). It is also sometimes determined by drying on a watch glass in a vacuum at ordinary temperature. Limits of 0.1 to 0.25 per cent. are usually specified.

For the determination of acidity, the trinitrotoluene is melted under water with stirring. The water is decanted and the extraction repeated twice. The water extract is tested either with litmus or by titration to phenol phthalein. The acid may include sulphuric and nitric acid, which are sometimes tested for separately, and organic acids (nitrocresols, etc.).

Tetranitromethane in crude trinitrotoluene may be estimated by reduction of hydrazine in alkaline solution to nitrogen

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"Liquid trinitrotoluene" is a mixture of isomeric trinitrotoluenes with some dinitrotoluene which forms a by-product in the purification of trinitrotoluene by crystallisation or centrifuging. It has a limited use in commercial explosives. Its melting point and other properties are very indefinite.

(d) Dinitrobenzene

$C_6H_4(NO_2)_2$. Mol. wt., 168; M.P., 90°; insol. water; soluble in organic solvents.

Dinitrobenzene is but little used. It is objectionable on account of its poisonous properties. The main ingredient is the meta-derivative, but the other isomers are also present, and the commercial product may give a setting point as low as 80°. It should be free from mononitrobenzene, which can be recognised by its smell.

(e) Trinitrobenzene

$C_6H_3(NO_2)_3$. Mol. wt., 213; M.P., 122°; insol. water; soluble in organic solvents.

Trinitrobenzene is also but little used. It forms additive compounds with amines and with naphthalene. It gives an intense red colour with alkalis in presence of alcohol.

(f) Nitronaphthalenes

These are used in various mixed explosives. They are usually met with in an impure form.

Mononitronaphthalene. The commercial product consists mainly of the alpha-compound. The pure compound melts at 61°. The commercial product should have a melting point of at least 56°. It boils at 304°. It is tested in the usual way for absence of acidity, insoluble matter, etc.

Dinitronaphthalene. This is a mixture of the 1.5-isomer (M.P. 217°) and the 1.8-isomer (M.P. 170°). It has an indefinite melting

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point, usually about 135° to 140°. It forms a dirty yellow to red brown crystalline powder. It gives a pink colour with alcoholic ammonia.

Trinitronaphthalene. This was used to some extent during the war in admixture with picric acid, etc. It is a mixture of various isomers and has no definite melting point. The melting points of the individual constituents are 1:3:8 (218°), 1:2:5 (113°), 1:3:5 (122°), 1:4:5 (154°). Some dinitronaphthalene is also present. The nitrogen percentage gives some indication of the proportion of trinitro-compound.

(g) Tetryl

Trinitrophenyl methyl nitramine $(NO_2)_3C_6H_4N(CH_3)NO_2$. Mol. wt., 287; sp. gr., 1.725; M.P., 131°; insol. water; soluble in organic solvents.

Tetryl forms a yellow crystalline solid. It should melt at 129° or above. It decomposes somewhat readily when molten and the setting point cannot be satisfactorily measured. It should leave only a trace of residue when dissolved in acetone and should be practically free from acid. In some countries a distinction is drawn between surface acid and that which is found by dissolving the tetryl in an organic solvent and adding water. Tetryl is much less soluble in carbon tetrachloride than trinitrotoluene; this is made use of for the separation of the nitro-compounds. Melting-point diagrams are also made use of to estimate the composition of such mixtures.

The nitramine nitrogen may be estimated by the nitrometer method. Tetryl is less stable than the majority of nitro-compounds. The stability may be estimated by the evolution of gas on heating in a vacuum (see p. 92).

(h) Other Nitro-compounds

Dinitrophenol $(NO_2)_2C_6H_3OH$. The pure 1:2:4 compound melts at 114°, commercial samples usually at about 110° to 112°. It has acid properties and forms salts. It should dissolve completely in cold dilute sodium hydroxide solution and in benzene, and should not contain more than 0.1 per cent. of organic chlorine. It should be free from lead. It is somewhat volatile in steam and can be separated from picric acid by steam distillation, though not very readily. The dinitrophenol in a mixture with picric acid may be estimated by bromination.

Trinitroanisole $(NO_2)_3C_6H_4OCH_3$. This is the methyl ester of picric acid and as such can be hydrolysed to picric acid by warm

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alkalis. The pure substance melts at 68°, the commercial product at about 65°. It should be free from mineral acids and from picrates.

Trinitroresorcinol (Styphnic acid) $(NO_2)_3C_6H_2(OH)_2$. This is an acid somewhat similar to picric acid in its general properties. It melts at 175.5°.

Trinitrochlorobenzene $(NO_2)_3C_6H_2Cl$. This has been very little used as an explosive, but serves for the preparation of other trinitro-compounds. It melts at 83°. The chlorine is very reactive and is readily replaced by the amino- or hydroxy-group.

Hexanitrodiphenylamine $(NO_2)_6C_6H_4.NHC_6H_4(NO_2)_3$. This compound melts at about 230°, but undergoes decomposition below the melting point. It is almost insoluble in most solvents, but dissolves in a mixture of acetone and pyridine, and the solution should leave very little insoluble residue. The compound has acid properties and forms salts of various metals.

2-4-6 Trinitrometaxylene $(CH_3)_2C_6H_3(NO_2)_3$. On nitration of commercial xylene, this product is obtained in admixture with *o*- and *p*-nitrated xylenes, especially dinitro-derivatives. The melting point of the crude explosive is 182°, and to lower the melting point the product is mixed with trotyl.

Hexanitrodiphenylsulphide $(NO_2)_6C_6H_4SC_6H_4(NO_2)_3$. The pure substance melts at 233°, the commercial product at about 225°. It is tested as usual for acids and other impurities.

Tetranitroaniline. Yellow crystals of M.P. 216°.

IV. SMOKELESS POWDERS

The composition of smokeless powders varies greatly, but they contain in general nitrocellulose, either completely or partially gelatinised. The completely gelatinised powders have a more or less horny structure; the partially gelatinised powders are porous, and can be comparatively easily broken down to powder. Many smokeless powders contain nitroglycerine, and most contain stabilisers.

Preparation of Sample. Gelatinised powders are ground in a mill of the coffee-mill type (see Abel Heat Test, p. 71). A small portion is passed through and discarded, and the main sample is passed through the sieves as used for the heat test. For general analysis, the material which passes through holes of 0.032 inch diameter is taken.

Some powders in the form of small flakes do not require grinding. Particles of iron may be removed from ground powders by a magnet. For the quantitative analysis the powder is dried at 60° to 70° to

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remove the solvent. Nitroglycerine powders should not be warmed for more than an hour at 60°. Alternatively, the volatile matter may be determined on a separate portion of the ground powder.

Qualitative Analysis

The nature of the gelatinising solvent can generally be detected by its smell. The powder should then be tested to ascertain whether it is a nitrocellulose powder or whether it contains nitroglycerine. It is digested for a considerable time with ether, decanted, and the solution allowed to evaporate in a dish. If a minute quantity of the liquid is absorbed on a piece of filter paper and struck on an anvil, an explosion occurs if the liquid be pure nitroglycerine. Apart from nitroglycerine, ether extracts stabilisers, nitro-compounds, etc. Camphor is detectable by its smell. Diphenylamine is recognised by the blue colour which it gives with sulphuric and nitric acids. On heating a solution of diphenylamine in 95 per cent. alcohol with a few drops of chlorine water, a green coloration is formed, changing slowly to dark violet on keeping or warming. Mineral jelly may be separated from nitroglycerine by boiling with 80 per cent. methyl alcohol. Substituted ureas and urethanes are also sometimes met with. The aqueous extract is examined for salts, and the ash is also tested.

Quantitative Analysis

Volatile Matter.—This includes the gelatinising solvent and water. In absence of volatile ingredients, such as nitroglycerine, the weighed ground powder may be dried by heating, and then reweighed. Temperatures of 65° to 100° are employed. It is of importance to avoid loss of volatile matter of the ground powder in the cold before weighing. For this reason the powder should not be too finely ground. Some heating takes place during the grinding. In some cases the powder is not ground, but is cut up into pieces, dissolved in ether-alcohol, reprecipitated by water, evaporated and dried in a vacuum at 50° or by heating to 95°-100°. The loss of weight, corrected for any residues in the solvent represents the volatile matter. The object of this procedure is to avoid initial losses of solvent. If a slightly volatile ingredient be present, the estimation may be made by drying at ordinary temperature in a vacuum.

In powders containing nitroglycerine, the volatility of the latter exercises a disturbing effect. To prevent escape of nitroglycerine, the apparatus shown in Fig. 2 is

It consists of an aluminium dish A
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and a conical glass-cover B, the whole apparatus weighing about 40 g. The ends of the sticks of powder are discarded and it is then ground as for the heat test. This should occupy one and a half to two minutes. Approximately 5 g. is weighed out into the dish, which is then covered with the cone, the whole accurately weighed and heated on an iron plate resting on a water bath. After three hours the apparatus is allowed to cool for half an hour in a desiccator, and weighed. The cone should rest closely on the rim of the dish to prevent loss of nitroglycerine. The nitroglycerine condenses completely on the glass cone. Separate determinations of water and organic solvent are not usually undertaken. Distillation with xylene has been used for the estimation of water. Dupré gave a method depending upon the reaction between water and calcium carbide. Pieroni proposed to subject the powder to steam distillation and estimate acetone in the distillate by conversion to iodoform.

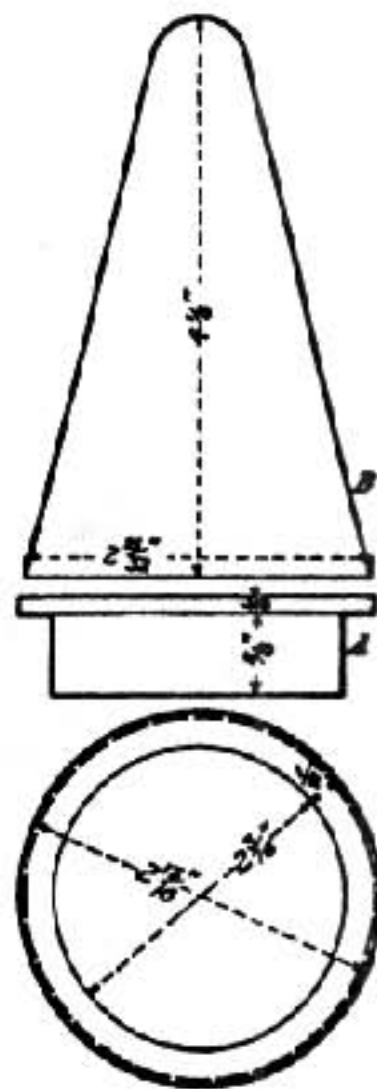


FIG. 2.

Chemical Analysis.—The powder is first extracted in a Soxhlet or other extraction apparatus to separate the nitroglycerine, etc. Pure dry ether should be used; sometimes a little chloroform (10 per cent.) is mixed with the ether to prevent solution of nitrocellulose. The solution is carefully evaporated and the flask is placed on a hot-plate surmounted by a sheet of uralite with holes which do not permit the flask to touch the hot-plate. From time to time the flask is removed and air, at ordinary temperature, is blown through it. This is continued until the weight becomes constant. The nitroglycerine, etc., may also be dried in a vacuum over calcium chloride.

A nitrogen determination may then be made by the nitrometer method. Care should be taken in introducing a solution of the substances in concentrated sulphuric acid into the nitrometer, as ether peroxide may give rise to heating and explosion in the bulb.

It is to be observed that the nitrogen determination may be

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disturbed by mononitrobenzene derivatives, as these are partially nitrated to dinitro-derivatives. Diphenylamine and other stabilisers also affect the results. As the Schulze-Tiemann method is rendered inaccurate by the volatility of the nitroglycerine, it has been proposed to hydrolyse a weighed quantity of the residue with alcoholic potassium hydroxide and estimate the nitrogen by ferrous chloride and hydrochloric acid.

In extracting nitroglycerine with ether and evaporating as above, slight losses of nitroglycerine occur by reason of its volatility. For this reason the nitroglycerine is sometimes estimated by difference. Silberrad, Phillips, and Merriman described a method in which the ether-extract is boiled with sodium ethylate to saponify the nitroglycerine, and the nitrogen reduced to ammonia by powdered zinc and iron.

Mineral jelly or paraffin may be separated from nitroglycerine by boiling with 80 per cent. methyl alcohol. This dissolves the nitroglycerine. The solution is filtered and the insoluble portion dissolved in ether, evaporated and weighed. Alternatively the nitroglycerine may be removed by saponification with alcoholic potassium hydroxide, and the solution diluted with water and extracted with ether.

For the separation of nitroglycerine from nitroaromatic compounds, Hyde gives a method depending on extraction with carbon disulphide and 65 per cent. aqueous acetic acid. Dickson and Easterbrook recommend separating nitroglycerine from nitro-compounds by dissolving the mixture in methyl alcohol and destroying the nitroglycerine by ferrous chloride solution, after which the solution is extracted with ether. Lutri hydrolyses the nitroglycerine with 20 per cent. sulphuric acid and extracts the nitro-compounds with benzene.

Camphor may be estimated according to Foerster by heating the powder with water on a water-bath and adding sodium hydroxide solution gradually. The heating is continued until the structure of the powder is destroyed. The camphor is distilled over with some of the water into a receiver of special design, in which it is treated

with a known quantity of benzene, and natural camphor determined by means of a polarimeter. A gravimetric method is described by Vieth and Bilhuber, in which the powder is hydrolysed as above and the camphor distilled over into a receiver containing ether. After

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repeated extractions with ether, the ethereal solution is dried with calcium chloride and a portion is evaporated.

For the estimation of *diphenylamine* the powder may be saponified as above, and then distilled until all the diphenylamine has passed over. The distillate is extracted with ether, which is separated, dried with calcium chloride and evaporated. The diphenylamine may also be estimated by conversion to tetrabromo-diphenylamine. For this purpose the ethereal solution is evaporated with alcohol, and excess of bromine is added to the alcoholic solution with stirring. The tetrabromo-diphenylamine separates out, and the supernatant liquor should be clear and should smell distinctly of bromine. Water is added and the whole is boiled to remove alcohol and bromine. The bromine compound is filtered off, washed with warm water and dried in a steam oven. The bromination may also be effected by potassium bromate and bromide in acid solution.

Urea derivatives may also be present. Diphenylurea (asymm.) is hydrolysed by strong sodium hydroxide solution and the resultant diphenylamine is estimated.

Centralite is converted to a dibromo-derivative on bromination and may be estimated volumetrically by the bromide-bromate method. Levenson brominates in alcoholic solution. Ellington and Beard use a carbon tetrachloride solution to avoid any interaction between the bromine and the solvent. The reagents consist of (1) 0.2 *N* bromide-bromate containing 5.568 g. potassium bromate and 30 g. potassium bromide per litre, and (2) 0.2 *N* thiosulphate. The propellant is extracted with ether in a Soxhlet using a 200 c.c. reaction bottle as receiver. The ether is then distilled off and the last traces are removed by a current of air. After cooling, 50 c.c. of pure carbon tetrachloride is added and the bottle shaken, whereupon 50 c.c. of bromide-bromate solution and 10 c.c. conc. hydrochloric acid are added. The bottle is shaken for five minutes and 20 c.c. of 15 per cent. potassium iodide added. After vigorous shaking, the solution is titrated with thiosulphate. A blank test is included.

A separation of diphenylamine from centralite may be effected by precipitation of tetrabromodiphenylamine in aqueous alcohol, in which dibromocentralite is soluble.

After the extraction of all soluble ingredients by means of solvents, the *nitrocellulose* remains behind, together with any mineral matter,

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and may be dried and weighed. If necessary the nitrocellulose may be dissolved in acetone (1 litre of acetone to 10 g. of propellant). After allowing to stand, the liquid is decanted and a further portion of acetone added. This is shaken, allowed to stand and decanted. The residue is filtered and the combined acetone solutions are poured into 5 volumes of 1 per cent. aqueous calcium chloride solution. The acetone is boiled off and the precipitated nitrocellulose is collected, washed with hot water, dried and weighed. Chloroform is sometimes used to precipitate the nitrocellulose. A nitrogen determination is made on the nitrocellulose. The nitrogen is also determined in the original powder. It is to be observed that substances such as diphenylamine, camphor, naphthalene, resins, etc., have a disturbing influence on the results of the nitrogen determination. The matter insoluble in acetone may contain carbonates, nitrates, graphite, cellulose, starch and mechanical impurities.

The *mineral matter* (ash) in smokeless powders is estimated by heating carefully in a porcelain dish with a few cubic centimetres of fuming nitric acid on a water bath and evaporating. The residue is then incinerated. Sand may be estimated in the ash by dissolving out the other constituents with warm hydrochloric acid. The ash is also examined for salts of potassium, sodium, calcium, barium and magnesium.

Mercury is estimated as in nitrocellulose. Dupré describes the

application of the spectroscopic method to smokeless powders. Hehner gives a method based on precipitation of the mercury by copper and conversion to mercuric iodide. Berkhout gives a method depending on the estimation as metallic mercury.

V. INDUSTRIAL BLASTING EXPLOSIVES

The explosives in use for mining, etc., consist of mixtures of a wide range of oxidising and reducing substances, and the methods of separation can be given only in outline. Some explosives are in the form of powder, others in gelatinous form; in the latter case the gelatinous mass should be cut into thin shavings with a horn spatula to facilitate extraction. Before the examination it is advisable to satisfy oneself that the explosive is reasonably safe to handle. A small portion should be rubbed vigorously in a porcelain mortar with a porcelain pestle.

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Qualitative Examination

Some indications can be obtained by the smell and appearance. Nitroglycerol and dinitrochlorhydrin have a faint odour. Some nitro-bodies such as mononitrotoluene have a distinctive smell. Charcoal and aluminium are distinctive in appearance.

A small sample should be extracted repeatedly with pure dry ether. After digesting and allowing to stand the ethereal solution is filtered off and allowed to evaporate in a warm place. A small drop of the residual liquid is absorbed on a piece of filter paper and hammered on an anvil. Nitroglycerine explodes with a sharp crack. Nitroglycerol and dinitrochlorhydrin behave similarly. Nitric esters give off oxides of nitrogen on gently warming with ferrous chloride and hydrochloric acid. The specific gravity may also be made use of if ether-soluble substances other than these esters are absent.

Camphor remains dissolved in the nitroglycerine and gives a distinctive odour. It can be extracted by carbon disulphide. Sulphur, paraffin wax and resins separate out from the nitroglycerine. Sulphur crystals may be collected and burnt, giving an odour of sulphur dioxide. Paraffin wax is insoluble in cold alcohol. Resins may be separated from nitroglycerine by means of 65 to 70 per cent. acetic acid in which they are insoluble. They can be saponified by boiling with soda solution, and are reprecipitated by acid.

Some aromatic nitro-compounds crystallise out from the nitroglycerine; in certain cases a separation may be effected by extracting the nitroglycerine with 90 per cent. alcohol, in which higher nitro-compounds are sparingly soluble. The nitroglycerine may also be dissolved in 65 per cent. acetic acid, and the nitro-compounds extracted with carbon disulphide.

The residue from the extraction with ether may contain salts, kieselguhr, charcoal, wood meal, nitrocellulose and some undissolved sulphur. The salts are identified by the ordinary reactions; most of them are extractable by water. Carbonates are dissolved by dilute hydrochloric acid with evolution of carbon dioxide. Collodion may be dissolved in ether-alcohol and gun-cotton in ethyl acetate or acetone. The residual ingredients may be identified to some extent microscopically. Starch is detected by the iodine reaction. Wood meal and charcoal may be removed by ignition, leaving such ingredients as kieselguhr, talc, etc.

In some cases salts may be separated by means of their difference in specific gravity, using heavy liquids such as chloroform and bromoform.

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The following list gives the specific gravities of the commoner salts which may be present:—

Salt.	Sp. Gr.	Salt.	Sp. Gr.
Ammonium alum (cryst.)	1.62	Manganese dioxide	5.03
„ chloride	1.52	Potassium alum	1.75

" nitrate	1.73	" chlorate	2.34
" perchlorate	1.87	" chloride	1.99
" sulphate	1.77	" perchlorate	2.52
Barium nitrate	3.23	" sulphate	2.66
Calcium carbonate (precip.)	2.72	Sodium chloride	2.17
" sulphate (anhydr.)	2.97	" nitrate	2.26
" " (hydrated)	2.32	" sulphate (anhydr.)	2.66
Magnesium carbonate	3.04	" " (cryst.)	1.46
" sulphate (cryst.)	1.68		
" " (anhydr.)	2.65		

In some cases the analysis can be simplified. Thus powdered explosives (ammonium nitrate and chlorate explosives) may be extracted directly with water to remove soluble salts, and the insoluble constituents may be filtered off and identified. Petroleum or mineral oil may separate out from some chlorate explosives. Wood meal remains in suspension. Trinitrotoluene is best extracted with acetone. Aluminium is easily recognisable. Calcium silicide remains behind as a black powder, and evolves silicon hydride on addition of hydrochloric acid. Paraffin wax separates from nitro-compounds on melting and forms a surface layer. Naphthalene is detectable by its smell. Such explosives may also contain small percentages of nitroglycerine.

Quantitative Analysis

In the analysis of nitroglycerine compounds, care should be taken to obtain a thoroughly well-mixed sample, as nitroglycerine may segregate. In sampling, the ends of cartridges should be discarded.

Moisture. This may be determined by evacuation over calcium chloride for twenty-four hours. When nitroglycerine, dinitroglycol, nitrobenzene, or nitrotoluene are present, the method given under Smokeless Powders (p. 50) may be used.

The hygroscopicity is sometimes of importance. It is determined by spreading a weighed quantity of the material on a flat dish, which is then placed under a bell jar over water. The increase in weight is determined at intervals. A control test on an explosive or other material of known hygroscopicity must be included, as the absorption of moisture is affected by the temperature. Hygroscopicity tests may also be carried out on cartridges.

Extraction. The explosive is extracted with pure dry ether in a Soxhlet extractor or a Gooch crucible (preferably in a continuous

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extraction apparatus). Condensation of water is to be avoided, as this would lead to solution of water-soluble salts. The ether extract, which contains nitroglycerine and allied substances, nitrobenzene and its derivatives, sulphur, oils, mineral jelly, paraffin wax and resins, is allowed to evaporate at about 40° to 45°, taking care to avoid loss of nitroglycerine, etc. Special care should be taken to avoid loss if nitroglycol be present. The evaporation is continued until the weight is constant.

If the nitroglycerine is suspected to contain compounds such as dinitrochlorhydrin, it may be examined by specific gravity, nitrogen content, chlorine content, refractive index. Nitrosugars increase the viscosity and lower the nitrogen content. Hoffman and Hawse give a polarimetric method for nitrosugars.

Tetranitrodiglycerine lowers the nitrogen content of nitroglycerine and is much less readily soluble in 65 per cent. acetic acid. It is also much more viscous than nitroglycerine.

With reference to the nitrogen determination in the nitrometer, it is to be observed that impure ether containing peroxides may give rise to explosions on mixing the extracted substances with sulphuric acid and under other conditions.

It is advisable to mix a small quantity of the extract with sulphuric acid to ascertain whether heat is evolved, and if so, the weighed quantity should be first mixed with sulphuric acid of moderate strength, cooling with ice. Strong sulphuric acid is then added slowly with similar cooling.

Mononitrobenzene and mononitrotoluene give rise to errors in the nitrogen determination, but higher nitro-compounds do not affect it. Naphthalene, diphenylamine, centralite, etc., disturb the nitrogen

estimation.

Becker gives a volumetric method for the estimation of nitroglycerine. A solution in acetic acid is boiled with ferrous chloride and hydrochloric acid, and the ferric salt is titrated with titanous chloride, using ammonium thiocyanate as indicator. This is also applicable to dinitroglycol.

Paraffin wax separates out from the nitroglycerine when the ether is evaporated off. It is pressed between filter papers and identified by its form and melting point. To determine its quantity the extract is melted and separated in a warmed separating funnel. Resin may be saponified by hot soda, reprecipitated with acid and weighed, or may be titrated with alcoholic potassium hydroxide, using phenolphthalein as indicator.

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The separation of nitro-compounds, camphor, diphenylamine, etc., from nitroglycerine is dealt with under Smokeless Powders (p. 52).

It is sometimes found convenient to remove the whole of the nitroglycerine by heating for several hours with alcoholic potassium hydroxide. Water and ether are then added, and the mixture shaken in a separating funnel. The ethereal solution is evaporated, and the residue consisting of paraffin, mineral jelly or mineral oils, is weighed. The aqueous solution is acidified with hydrochloric acid and bromine is added to oxidise any sulphur. Any separated resin is filtered off and weighed, and sulphur is determined in the filtrate as barium sulphate. Sulphur may also be separated from nitroglycerine by 65 to 70 per cent. acetic acid.

Material Insoluble in Ether. This is dried at a moderate temperature and carefully transferred to a glass dish. It is then further dried at 80° to 90°, or if ammonium nitrate is present, at 70°. If it is in the form of an agglomerated mass, it should be roughly subdivided before drying. Sulphur, if present, may be extracted with carbon disulphide. The residue is then extracted with successive small quantities of water. Warming is sometimes necessary, particularly for the extraction of potassium perchlorate. On the other hand, if aluminium and ammonium nitrate are present, warming must be avoided, or interaction may occur. In addition to salts, the aqueous extract may include soluble matter from wood meal, which may contain as much as 3 per cent. of soluble substances.

Acids resulting from the decomposition of nitroglycerine may form soluble salts by interaction with calcium carbonate, etc. The various salts are estimated by the usual analytical methods. If perchlorates or other salts containing chlorine are present in conjunction with ammonium salts it is not permissible to remove the ammonium salts by direct heating, as this may lead to losses of chlorine. The residue insoluble in water is extracted with dilute hydrochloric acid to dissolve calcium carbonate, magnesia, zinc oxide and metals. If starch is present it should be hydrolysed by boiling with dilute acid.

The residue remaining insoluble in dilute acid may contain insoluble salts, kieselguhr, wood meal, etc. If nitrocellulose is present, the residue is shaken with ether-alcohol to determine the collodion. The ether-alcohol solution is allowed to settle, and an aliquot portion is withdrawn and evaporated. Gun-cotton, if present, is dissolved in acetone, and the solution evaporated. Acetone dissolves certain constituents of wood meal; errors due to this may be avoided by evaporating the acetone solution to 20-25 c.c. and diluting with 100 c.c. of hot water, which precipitates the nitrocellulose. The residue is washed several times with the solvent and finally dried

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and weighed. It is thus also possible to determine the nitrocellulose by difference.

The insoluble residue may contain charcoal and other carbonaceous matter such as wood meal, etc. These are removed by incineration, and the residual ash contains mineral matter such as kieselguhr.

Nitrostarch is somewhat soluble in ordinary ether containing small quantities of alcohol. For this reason petroleum ether is sometimes

used to extract oils, resins and sulphur. The insoluble portion is extracted with water to remove soluble salts and the nitrostarch is then separated from insoluble matter by means of acetone.

In some cases the analysis can be shortened (ammonites, chloratites). A weighed quantity is digested with acetone which readily dissolves nitro-compounds, nitroglycerine and hydrocarbons. The insoluble residue is further tested as above, the salts being extracted with water, and the insoluble residue examined for wood meal, charcoal, aluminium, silicides and mineral matter.

VI. INITIATORS

(a) Mercury Fulminate

$\text{HgC}_2\text{N}_2\text{O}_2$. Mol. wt., 254.6; sp. gr., 4.42; soluble in 100 parts water, 0.07 at 12°, 0.77 at 100°.

Mercury fulminate forms a white to greyish-brown crystalline powder. It is still the most important initiatory explosive. It is very sensitive to shock or friction and must be handled with great care. Goggles should be worn and should be tested beforehand to ensure their resistance to explosive shock. On heating, it explodes at about 150° to 160°, but may explode on more prolonged heating at 100°. The influence of heat in a vacuum on mercury fulminate under various conditions has been exhaustively investigated by Farmer. Mercury fulminate is insoluble in most organic solvents, but dissolves with decomposition or formation of double compounds in ammonia, iodides, cyanides, thiocyanides, thiosulphates, pyridine, etc.

Mercury fulminate should be at least 98 per cent. pure. It should be neutral, practically free from oxalates, chlorides and metals other than mercury.

The moisture is determined by drying over calcium chloride in a desiccator at ordinary temperature and pressure.

In the determination of the insoluble matter the solvent used may be either pyridine, or an aqueous solution of sodium thiosulphate or

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potassium cyanide. The residue should be carefully dried to avoid loss of mercury by volatilisation.

Free mercury may sometimes be detected as tiny globules. A more sensitive test is to warm the fulminate in a test tube in which a strip of gold leaf is suspended. Metallic mercury shows itself by the formation of spots of amalgam on the gold leaf. For the quantitative estimation, the residue insoluble in pyridine is treated on a filter with a solution of 3 g. potassium iodide and 6 g. sodium thiosulphate in 50 c.c. water. This converts any organic mercury compounds to mercuric iodide, which is soluble in thiosulphate. The insoluble matter is dried at 80° to 90° and weighed. This is taken as mercury. Nicolardot and Boudet shake the fulminate with a 5 per cent. solution of ammonium hydrosulphite and report the residue as metallic mercury.

The fulminate value is best determined by the method of Brownsdon. For the determination, 0.3 of the sample is wetted with about 5 c.c. of water, and 50 c.c. of a solution containing 6 per cent. KI and 2.5 per cent. $\text{Na}_2\text{S}_2\text{O}_3$ (cryst.) is added. The mixture is shaken for about a minute and then neutralised to methyl orange with *N*/10 HCl. The solution and titration should not occupy more than about three minutes as the titre alters rapidly. For the calculation 4HCl is equivalent to $\text{HgC}_2\text{N}_2\text{O}_2$.

The total mercury may be estimated, if required, by precipitation with ammonium sulphide. Losanitsch described an electrolytic method.

Oxalates are estimated by dissolving the fulminate in ammonia, precipitating with ammonium sulphide and determining the oxalate in the filtrate. Alternatively the fulminate may be dissolved in 20 per cent. ammonia and acetic acid added to precipitate most of the fulminate. The oxalate is then determined in the filtrate. According to Rathsburg, mercury fulminate should not decolorise *N*/50 permanganate.

(b) Lead Azide

$\text{Pb}(\text{N}_3)_2$. Mol. wt., 291; sp. gr., 4.80; soluble in 100 parts water, 0.03

at 18°, 0.09 at 80°; sparingly soluble in organic solvents.

Among the initiating explosives lead azide is second in order of importance. It forms fine white crystals, but these tend to increase in size in contact with water and may explode spontaneously. On heating it explodes at 320° to 340°.

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The content of lead azide should be at least 95 to 97 per cent. Usually a little basic azide is present, and this is sometimes preferred, as it is stated to render the material safer. Metals other than lead should be present only in traces. The lead azide should dissolve practically completely in dilute nitric acid. It should be free from acid.

The moisture is determined by drying over calcium chloride or sulphuric acid.

The total lead content may be estimated by evaporating with sulphuric acid on a water bath, and then gradually heating more strongly.

The azide value may be determined by shaking with dilute nitric acid until dissolved and precipitating as silver azide with excess of standard silver nitrate. A little sodium acetate is added to decrease the solubility of the silver azide. The excess of silver nitrate is titrated with thiocyanate. The hydrazoic acid may also be distilled off after addition of acetic acid or ammonium nitrate and estimated as silver azide.

Gasometric methods are also sometimes used.

Azides and hydrazoic acid may be detected qualitatively by the red colour which they give with ferric salts.

Among other substances suggested as initiators are tetrazole derivatives, cyanuric triazide, lead trinitroresorcinate, hexamethylene triperoxidodiamine and others. Normal lead dinitrosalicylate has a sensitiveness to shock substantially equal to that of mercury fulminate.

(c) Detonator and Cap Compositions

(i) Detonator Compositions. If the composition is contained in a metal capsule, great care is necessary in the removal of the contents, as the materials are very sensitive. It is advisable to carry out the operation by mechanical means from behind a steel screen. In some cases the detonator is cut open, in others it is squeezed with pliers under precautions to loosen the contents which are then tipped out. The composition may also be loosened by rolling the detonator carefully between two pieces of smooth hardwood board. In opening electric detonators, Taylor and Rinkenbach recommend cutting into the sulphur filling and asphalt and then peeling the copper down in a spiral until the plugs are loosened enough to be withdrawn easily.

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The portion of the shell containing the charge should on no account be cut into.

It is of importance to observe whether the contents of a detonator consist of one layer of composition or whether they have also a separate layer of a nitro-compound. In the latter case the two layers should be separated mechanically as completely as possible. The approximate weight of the filling should be determined.

The moisture content is not usually determined; it is generally very low. The efficiency is, however, strongly affected by moisture, and the estimation may be made, if required, by drying for three days over sulphuric acid in a vacuum desiccator. A small beaker of mercury should be inserted to prevent evaporation of metallic mercury from fulminate.

The analysis of simple fulminate-chlorate mixtures may be effected by extraction either with water or with pyridine. In the former method the mixture is digested with cold water, and the residue is washed on a filter. The mercury fulminate is dried at 50° for three hours and weighed. Some fulminate dissolves in the water. This is estimated by precipitation as sulphide. The chlorate may also be determined in the filtrate. The solution is boiled with nitric acid and then treated with formaldehyde and silver nitrate. Silver chloride is precipitated and the estimation may be made gravimetrically or by Volhard's method.

Mercury fulminate is soluble in pyridine and may be extracted,

leaving the chlorate undissolved. The latter is washed with ether, dried and weighed. Small quantities of impurities in the fulminate remain undissolved; these may be separated from the chlorate by extraction with water. The fulminate may be separated as sulphide after diluting the pyridine solution with water.

Binding material may be present in small quantities and is estimated by difference.

In the analysis of composite detonators containing fulminate-chlorate with tetryl or trinitrotoluene the two layers are separated mechanically; the fulminate-chlorate is dealt with as above, and the nitro-compound is examined for melting point, acidity and possibly nitrogen content. If it is not found possible to separate the two layers satisfactorily, composite tetryl detonators may be dealt with as follows: The contents of two or three detonators are extracted with water, which dissolves the chlorate and a little fulminate. These are estimated in the aqueous solution as above. The filter and its contents are dried for five hours at 70° and weighed. The fulminate is dissolved out with warm 30 per cent. hydrochloric acid, followed by five washes with water. The residue is dried for three hours at 110° and weighed. If it is required to estimate insoluble impurities, the tetryl may be dissolved in acetone or benzene.

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In the examination of composite detonators containing lead azide in conjunction with trinitrotoluene or tetryl, the primary and secondary fillings are separated mechanically and tested. If it is not found possible to separate the two layers they are mixed together and the nitro-compound is extracted with absolute ether, orthonitrotoluene or other suitable solvent. The insoluble lead azide is dried at 70° and weighed. If lead trinitroresorcinate is also present, the content of lead and of azide-nitrogen is determined.

(ii) *Cap Compositions.*—Percussion caps are required for ignitory purposes in fire-arms and thus differ from detonators. Antimony sulphide is frequently added for this purpose. Ignitory compositions are much more varied in nature than detonator compositions and are often complex in character. Mercury fulminate is frequently used as a constituent, but some are free from fulminate.

The compositions are very sensitive, but the charge is much smaller than in detonators, and consequently they can be handled without serious risk. It is usually necessary to extract the charges of several caps to obtain enough material for the tests. The hands should be protected by heavy gloves or cloth.

The compositions vary so much that a general scheme for the identification of ingredients cannot be given.

The weight of charge is determined by emptying a sufficient number of caps and weighing them before and after emptying. If tinfoil is present, the small discs are carefully cleaned and weighed with the empty caps. Moisture is not usually determined; if necessary it may be estimated by drying in a vacuum over sulphuric acid.

A simple cap composition containing mercury fulminate, antimony sulphide, potassium chlorate and glass powder may be analysed by successive extractions with warm pyridine to dissolve fulminate and shellac, water to dissolve potassium chlorate, hydrochloric acid or aqua regia to dissolve antimony sulphide. Glass powder remains undissolved. The mercury, antimony and chlorate may be determined in the extracts.

The following method is given by Taylor and Rinkenbach for single primers. The fulminate is estimated by the thiosulphate

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method (see under Mercury Fulminate, p. 60). After the titration the supernatant liquor is decanted through a filter, and the antimony sulphide washed five times with hot water by decantation. The filter is dried and the sulphide on it is dissolved with hot hydrochloric acid, the filtrate being collected in the dish containing the bulk of the antimony sulphide. This is heated to expel hydrogen sulphide. About 1 g. of tartaric acid is added and the solution is transferred to an Erlenmeyer flask. Ammonia is added until the solution is nearly

neutralised, but no excess should be added. The neutralisation is completed with solid sodium bicarbonate and an excess of 0.05 g. is added. The solution is then titrated with *N*/100 iodine solution and starch.

If ground glass is present, it remains as an insoluble residue which may be determined. The potassium chlorate is determined by difference. Heaven precipitates the mercury from the thiosulphate solution as sulphide, reduces the chlorate with ferrous sulphate and titrates the chloride formed.

Taylor and Rinkenbach give a method for such compositions, in which a sample is heated with dilute sulphuric acid and the sulphides of mercury and antimony are precipitated with hydrogen sulphide. The filtrate is evaporated, the chlorate being decomposed. The evaporation is completed in a platinum dish, and the residue is finally ignited. The potassium sulphate is weighed. The sulphides are dissolved in hydrochloric and nitric acid with addition of tartaric acid. Glass powder remains undissolved and is filtered off. The sulphides are again precipitated and separated by ammonium sulphide. The mercury is determined as sulphide, and the antimony solution is oxidised with nitric acid.

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VII. PHYSICAL AND EXPLOSIVE TESTS

The chemical analysis of explosives is frequently supplemented by physical tests. These may be combined with storage trials at ordinary temperature or under warm conditions to find whether alterations have taken place with regard to hardening, conglomeration, exudation, absorption of moisture, efficiency or stability.

Density. The method for gun-powder and similar powders is given on p. 30. The density of blasting explosives in cartridge form may be estimated by weighing and measuring the cartridges. Another approximate method is to measure the displacement of sand. A glass tube is filled with sand and weighed. It is then emptied and a weighed stick of the explosive is inserted. Sand is poured in until the tube is full. The sand is levelled off and the whole is weighed. The apparent density of the sand is determined separately in the same tube.

Tendency to Segregate. Mixed explosives may tend to separate to some extent into their ingredients by shaking or by alternations of moisture in the atmosphere. The effect of shaking may be determined by putting a quantity of the explosive into a wide-mouthed bottle, so that the bottle is partially filled. The bottle is corked and shaken in a mechanical shaker for an hour. The explosive is then examined for visible signs of segregation and separate portions may be taken out and examined for differences in ease of ignition, etc. The effect of moisture is ascertained by exposing a sample in a flat dish for alternate periods of twenty-four hours to moist and dry air and examining after a week for efflorescence of crystals.

Movement of nitroglycerine in a cartridge by gravitation is tested by keeping the cartridge in a vertical position for some weeks at 32°. Portions from the two ends are examined for nitroglycerine content before and after the test, which may be carried out in dry or moist air.

Exudation. This refers mainly to nitroglycerine explosives. Exudation is undesirable, as the liquid nitroglycerine which exudes out may become exploded by friction or shock. The exudation can be measured by placing a cylinder of the explosive on porous paper in a warm oven and ascertaining the amount of liquid which sweats out. A typical explosive is taken as a control. In a test prescribed by the Home Office, a cylinder is cut from the cartridge, such that the length is about equal to the diameter. The ends are cut flat and the cylinder is placed on a flat surface and secured by a pin. It is then kept at 85° to 90° F. for six days and nights. The cylinder must not decrease by more than a quarter of its height, and the upper surface

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must retain its flatness and the sharpness of its edges. Sometimes pressure is applied to facilitate the exudation, and centrifuging has also been applied. To test the exudation due to freezing, the cartridges are frozen and thawed three times. Exudation is also met with in

nitro-compounds which form eutectic mixtures.

Inflammability. A small sample of the explosive is filled into a glass or paper tube about 2 cm. in diameter. The exposed surface is smoothed, and a slow fuse is brought in contact with it and ignited, to ascertain whether the explosive inflames and whether it burns partially or completely. The test should be repeated on several samples. The ease of inflammation may also be measured by playing a small bunsen flame on to the explosive for a measured time, say ten seconds. Considerable differences are observed between different explosives. Control samples of known explosives should be included for comparison. Another method is to fasten a small quantity of the explosive to the end of a pendulum which swings through a flame in such a way that the time can be measured.

If the explosive has withstood the test in which it is exposed to the flame from a slow fuse, it is further tested by dropping a portion of 0.5 g. into a red-hot iron basin 12 cm. in diameter. The quantity may be increased to 5 g. if no explosion occurs. The basin must be well cleaned after each test and should be frequently renewed; on the other hand a new basin does not give quite normal results, until it has been used once or twice.

In some cases, larger quantities of a pound or two are burnt in a wood fire to ascertain the degree of danger to which the explosive may give rise in case of fire. The observations should be made under precautions at a safe distance.

Ignition Temperature. This is usually determined by placing 0.1 g. of the explosive in a small test tube, which is then corked and placed in a fusible metal bath at 100°. The temperature is raised 5° per minute until inflammation or explosion occurs. The quantity and rate of heating differ in different countries.

Sensitiveness to Shock and Friction. The sensitiveness to blows is measured by the falling weight test. The explosive must be finely divided and well dried. A small portion is spread in a thin layer on an anvil. A bolt rests on the explosive and a cylindrical weight is allowed to fall upon it from a measured height. If explosion occurs the test is repeated with a lower height of fall until the mean height is found at which explosion just occurs. A standard explosive which can be obtained in pure condition, such as picric acid, is taken as a control. Considerable difficulty has been met with in obtaining

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reproducible results. An improved method was introduced by Rotter in which the results of each impact are evaluated, not by personal judgment but by a quantitative measurement of the gas produced by the decomposition of the explosive. A number of typical results are quoted by Robertson. The sensitiveness to friction may be tested qualitatively by rubbing a small portion of the explosive vigorously in an unglazed mortar with an unglazed pestle. A useful test is to strike a glancing blow with a mallet, the explosive being laid on anvils of different materials. A broomstick may also be used, the explosive being struck with the end by a blow in which the broomstick is moved in the direction of its axis at an angle of about 60° to the anvil. A more scientific test on these lines is described by Howell. His apparatus consists of a steel anvil with grooves to hold the

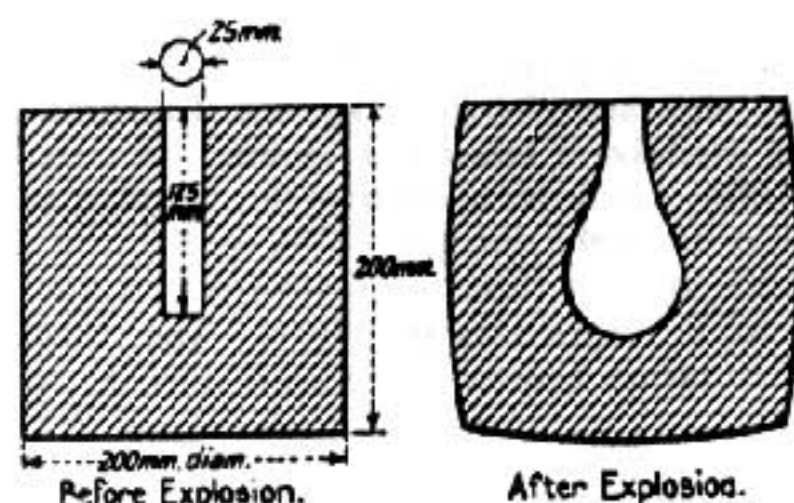


FIG. 3.

explosive (7 g.), and a swinging shoe which is allowed to fall with a

circular motion from various heights.

Lead Block Test. This is one of the oldest tests for the explosive power, and is still widely used. The explosive is fired in a cavity in a cylindrical lead block. The cavity becomes enlarged and the increase of volume is taken as a measure of the power. Standard conditions were laid down at the Fifth International Congress of Applied Chemistry. The lead block (Fig. 3) is cylindrical and is 200 mm. in height and 200 mm. in diameter. The cylindrical cavity is 125 mm. deep and 25 mm. in diameter. Ten g. of explosive wrapped in tinfoil is taken for the test, and tamped with sand. The charge is fired by a detonator, and the expansion is measured by finding the volume of water necessary to fill the cavity. The original capacity of the bore is deducted and allowance should be made for the expansion due to the detonator. The purity of the lead and the temperature

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of casting of the blocks affect the results to some extent.

Ballistic Pendulum. A heavy mortar is suspended from a bearing and a stemmed shot is fired into it from a steel gun. The degree to which the pendulum swings gives a measure of the energy imparted to it. The weight of the mortar and height of suspension differ in different countries, e.g. at Rotherham 5.025 tons at 92 in., in America 14.1 tons at 89.75 in. The gun is brought to a measured distance from the mortar and fired electrically. Charges of $\frac{1}{2}$ to $\frac{1}{4}$ lb. of explosive are used, and a standard explosive is taken for comparison.

In another method a heavy mortar, firing at an elevation of 30°, is used. The explosive is detonated by means of a slow fuse and propels a projectile weighing 15 kg. The distance to which this is thrown is measured.

Brisance Meter. In using this apparatus, the violence of the explosive effect is measured by the crushing of a metal cylinder. The explosive is detonated on a steel plate, covered by two lead discs for protection. The steel plate is 2 cm. thick, weighs 320 g. and is supported by a piston fitting into a hollow steel cylinder. The lower end of the piston rests on a copper cylinder supported by the steel base. The detonation of the explosive transmits a pressure through the piston to the copper cylinder, and crushes it to an extent which can be measured. The degree of crushing is used to compare the brisance of different explosives.

Rate of Detonation. Two methods are in use. In the direct method, the time of detonation of a measured length of a column of explosive is determined. This necessitates the accurate measurement of very short time intervals, which is effected by means of a rapidly rotating drum fitted with a speed recorder. The column of explosive is fitted with wires at a fixed distance apart, generally one metre. The rupture of the wires gives rise to induction sparks, which give spots on the smoked surface of the drum. By measuring the distance between the spots, the rate of detonation can be calculated. The velocity depends upon the diameter of the train of explosive up to a limiting value, the degree of confinement, the density, and the method of initiation.

An alternative method is that of Dautriche. This method is a comparative one and necessitates a knowledge of the rate of detonation of a standard explosive enclosed in a detonating fuse. The explosive to be tested may be in cartridges or compressed into a tube; a detonator is inserted at one end (Fig. 4). Two other detonators are inserted into the sides of the tube at a known distance apart, and connected to a loop of the detonating fuse. When the explosive is

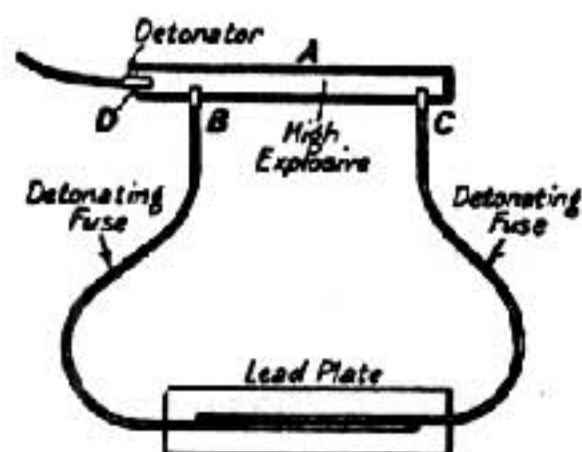
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detonated the detonation is transmitted successively to the two ends of the detonating fuse, and the two waves meet at a point depending on the rates of detonation of the main explosive and of the explosive in the detonating fuse. The point at which the waves meet is ascertained by the indentation of a slab of lead on which the detonating fuse lies.

The sensitiveness to detonation is determined by subjecting the explosive in its usual form (e.g. in cartridges) to the action of detonators of different intensities. These are fired electrically, and the effect on

the explosive is observed.

In order to ascertain the propagation of detonation, two cartridges are placed end to end on the ground at a certain distance apart, and one of them is detonated. By varying the distance it can be ascertained at what distance the first cartridge is able to detonate the second.



Length and Duration of Flame. These are of importance in connection with the ignition of fire-damp, etc. The measurements are made photographically. A sensitive film is fixed to a drum, which is rotated at a known speed, and the flame is photographed through a narrow slit in such a way that the height of the image shows the length of the flame and the breadth shows its duration.

Testing of Detonators. The initiating action may be determined by the Esop and Wöhler tests in which the detonator is fired in contact with an explosive which has been partially deadened by the addition of an inert substance. Tests are also made to determine the limiting charge of a detonator composition, which just suffices to bring about detonation. In the "Sand test" of the U.S.A. Bureau of Mines, a detonating charge is exploded in a mass of carefully graded sand and the degree of pulverisation caused by the explosion is measured.

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In the "Nail test" the detonator is attached by means of wire to a nail, the two being parallel and the lower end of the detonator being level with the centre of the nail. The power of the detonator is measured by the degree of bending of the nail. Standard nails must be used for the test.

The Trauzl test is sometimes used with a smaller lead block. The indentation of a lead plate is also frequently made use of. Methods for caps are given by Brownsdon. These include photographs of the flash with the help of a revolving perforated disc, to determine the length and duration of flash, measurements of the heat evolved and the volume of gas generated, in a special apparatus.

C. STABILITY TESTS

Nitric esters undergo gradual decomposition on storage. Stability tests are therefore necessary as a control of the safety of explosives of this type. The tests are applied during manufacture and to the finished explosive; and they may also be applied at intervals during storage, especially in hot climates.

The usual procedure in stability tests is to subject a sample of the explosive to a raised temperature in order to increase the rapidity of the decomposition and obtain a quick indication of the stability. After heating at constant temperature for a certain length of time, the degree of decomposition is measured by one of the following methods:—

- (1) By indicators depending on the action of nitric peroxide.
- (2) Direct observation of brown fumes.
- (3) Measurements of spontaneous heating.
- (4) Methods depending on the explosion of the sample.
- (5) Quantitative estimations of decomposition products.
- (6) Loss of weight.
- (7) Gasometric methods.
- (8) Acidity measurements.

The most reliable procedure is to carry out a heating trial at a temperature not far removed from the temperature of storage, but this necessitates a prolonged trial in order to bring about a measurable degree of decomposition, and is not always practicable.

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I. STABILITY TESTS DEPENDING UPON INDICATORS FOR NITRIC PEROXIDE

(a) Abel Heat Test

This is the oldest test, but is still widely used. It depends upon the colorimetric estimation of traces of nitrous acid or nitric peroxide by test papers prepared with potassium iodide and starch. The explosive is contained in a test tube which is heated to a constant temperature, the test paper being suspended over the explosive.

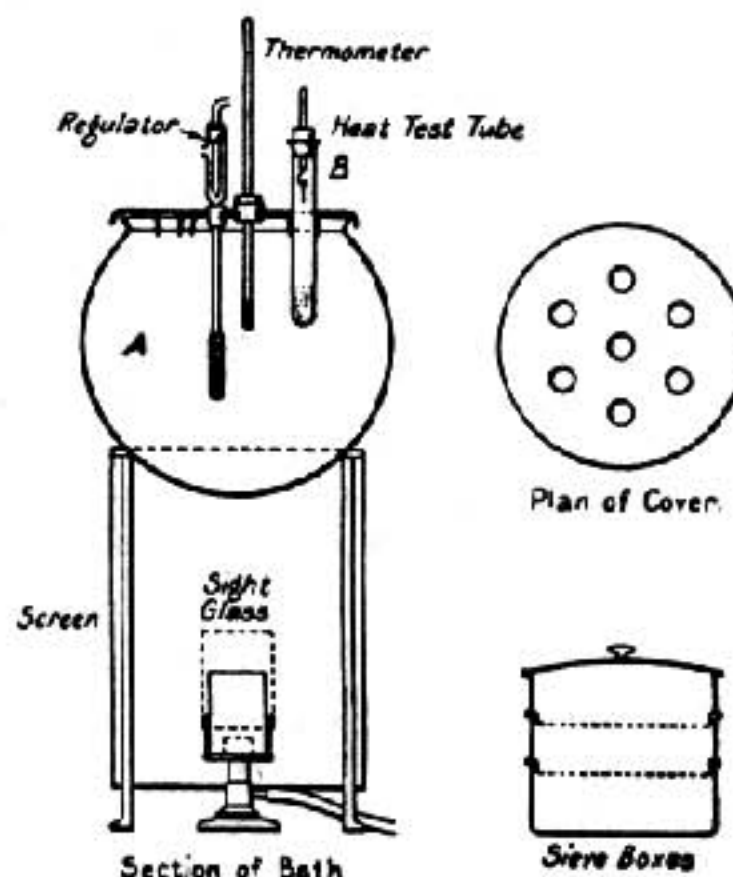


FIG. 5.

The following are the main requirements. Apparatus of the standard patterns can be obtained from chemical apparatus dealers.

Heating Bath (Fig. 5). The bath consists of a spherical copper vessel $7\frac{1}{2}$ in. diameter with an aperture of $5\frac{1}{2}$ in. It has an overflow pipe $\frac{1}{2}$ in. below the top. The lid is of copper about 6 in. in diameter and has 7 holes, one for a thermometer and six for the glass tubes. These are held in position by wire supports fixed to the lower side of the lid. The bath rests on a tripod stand surrounded by a screen, and is heated by an Argand burner with a copper chimney.

Test Tubes. These are of glass, without lips, and are $5\frac{1}{2}$ to $5\frac{3}{4}$ in. in height. They are of such diameter that they will hold 20 to 22 c.c. of water when filled to

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a height of 5 in. They are etched with short lines at 3, $3\frac{1}{2}$ and 5 in. from the bottom. Rubber rings are provided which fit round the test tubes and rest on the bath lid.

Rubber Stoppers. These fit the test tubes; they are perforated and carry a glass rod, terminating at its lower end in a platinum hook to hold the test paper.

Dropping Bottle. This is for moistening the test papers with glycerine water. It is of brown glass and has a glass stopper which is drawn out to a thin-pointed rod, which dips into the liquid.

Lead Discs. To cover any holes in the lid which are not occupied.

Caps for Test Tubes. These are of black paper; they are of cylindrical shape and fit loosely over the tubes to exclude light. They have holes near the top and bottom to permit of convection of air.

Cordite Mill. This is of the coffee-mill type with a fluted grinding surface.

Cordite Cutter. A standard pattern of knife of the lever type is prescribed for cutting up cordite, etc.

Sieves. A circular brass or copper nest of sieves of standard dimensions is used. Ground cordite is collected between two sieves, consisting of sheets of brass drilled with holes 0.08 and 0.032 in. in diameter respectively. The lower sieve fits into a circular box, and the upper sieve has a domed lid.

Rectangular Sieve (for nitrocellulose). A brass frame of internal dimensions $7\frac{1}{2}$ in. by $5\frac{1}{2}$ in. is covered with tinned brass wire gauze with 10 meshes per inch.

Test Papers. These are prepared by dipping filter paper in a solution of starch and potassium iodide. The sensitiveness depends so much upon the paper used and the conditions of preparation that it is advisable to obtain them from a standard

source.

The test papers are prepared as follows: 220 c.c. of freshly distilled water is placed in a flask of Jena glass and raised to boiling over a spirit lamp burning pure spirit. Three g. of pure starch (cornflour) previously purified by washing six times by decantation with pure water and carefully dried, is suspended in 30 c.c. of pure water and poured into the 220 c.c. of boiling water with continuous shaking. The whole is boiled gently, with shaking, for five minutes. The starch solution is then added to a solution of 1 g. of pure potassium iodide in 250 c.c. of freshly distilled water. After standing overnight in a dark room, the clear supernatant liquid is carefully syphoned off and used at once for dipping the paper. The filter paper should be of pure cotton cellulose, free from size or loading and from all trace of impurity. The prescribed thickness is 0.18 mm. Sheets of the paper are passed singly through the iodide starch solution, which is contained in a porcelain tray. Each sheet is then held vertically over the tray, and excess solution is removed from the edges by a glass rod. The sheets are then hung up to dry in the dark. They are afterwards cut into strips 1 cm. by 2 cm., the edges of the paper being discarded. Freedom from laboratory fumes is essential in all these operations. The papers are allowed to mature for a month or more in the dark before use. They are preserved in brown glass bottles. To confirm that test papers are still serviceable after keeping, a drop of dilute acetic acid is placed on the paper; this should give no coloration for some time.

Standard Tint Papers. 0.48 g. of the finest yellow ochre, 0.2 g. of raw umber and 5 g. of fine gum arabic all finely ground are shaken with 100 c.c. of cold water until the gum has dissolved. The suspension is then well shaken and allowed to stand for an hour. Lines are ruled on filter paper with this suspension which is then cut up into strips 1 cm. by 2 cm. The breadth of the line must be between 0.5 and 1 mm.

Preparation of Samples for Test. Great cleanliness of the hands and all apparatus should be observed. Undue exposure of the

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explosives to light should be avoided in all the operations, and the test should be carried out without delay when the sample is prepared.

A. Explosives of Class 3, Nitro-compound, Division I

1. *Dynamite and other Nitroglycerine Preparations from which the Nitroglycerine can be extracted by Water as below.* A glass funnel (5.5 cm.) is fitted with a filter paper. The explosive is loosened from its cartridge; 13 g. is placed in the funnel and pressed down fairly tightly with a flat-ended glass rod. The funnel is placed in a heat-test tube and filled up with distilled water. The stem of the tube must not touch the side of the heat-test tube. The water displaces nitroglycerine from the dynamite, and when 2 c.c. of nitroglycerine have collected in the tube the extraction funnel is removed. No water must pass into the heat-test tube. The sample is then ready for heat test.

2. *Carbonite, Monobel Powder, and similar Friable Nitroglycerine Preparations from which the Nitroglycerine cannot conveniently be extracted as above.* The contents of the cartridge are loosened, and 3.2 g. weighed into a scoop and transferred by means of an aluminium funnel to a heat-test tube, collected at the bottom by tapping gently and pressed down to a height of 3 cm. with a flat-ended glass rod.

3. *Blasting Gelatine, Gelatine Dynamite, Gelignite, and Analogous Preparations.* The wrapper is opened, about half an inch of the end of the cartridge is cut off and discarded, and a portion weighing approximately 3.2 g. then cut off, avoiding contact with the hands. The portion is placed on the scoop and the weight is adjusted to 3.2 g. This is then transferred to a mortar and 6.5 g. of French chalk added. The explosive and French chalk are worked together with the pestle. This should require a half to one and a half minutes. The mixture is then ground by a circular movement of the pestle for half a minute, and should then be homogeneous in appearance. The mixture is transferred to a heat-test tube with the help of a horn spatula and aluminium funnel, and gently pressed down with a flat-ended glass rod to a height of 5 cm.

4. *Cordite, Ballistite and other Propellants of Class 3, Nitro-compound, Division I.* (a) Explosives in the form of sticks or tubes. The sticks or tubes are wiped with clean filter-paper and are cut into small pieces about $\frac{1}{2}$ in. long with the cordite knife, $\frac{1}{2}$ in. being rejected from each end of the stick or tube. The set of sieves is placed under the mill, and the cut sample is ground. The first portion is rejected and a sufficient quantity of the sample is to be taken to ensure that

the portion collected between the two sieves will suffice for the test. The nest of sieves is closed and shaken for one minute. The material

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collected on the second sieve is taken for the test, except that when the nominal diameter of the sticks or tubes is less than 0.03 in. the material from the bottom compartment is to be taken for the test. 1.6 g. is weighed out in the scoop, transferred by means of an aluminium funnel to a heat-test tube and shaken down by tapping the tube with the fingers.

(b) Explosives in the form of grains for small arms: 1.6 g. is weighed into the scoop and transferred by an aluminium funnel to the heat-test tube. Three such samples are weighed out.

B. Explosives of Class 3, Nitro-compound, Division 2

1. *Nitrocellulose Pulp.* Six thicknesses of filter paper are laid on top of one another. Sufficient of the sample to give about 5 to 6 g. after the final pressing is spread on the top sheet. Six other thicknesses of filter paper are similarly laid over the sample. The whole is then placed under pressure (e.g. in a hand-screw press) for about three minutes. The sample is then removed, rubbed up by hand on the filter paper and again pressed for three minutes on fresh filter paper. It is then transferred to the rectangular 10-mesh sieve and rubbed through it with the hand. Five g. is weighed out and spread evenly on an aluminium tray. The tray is placed in the oven, which should be at 120° F. (48.9° C.), and is kept there for fifteen minutes with the door closed. It is then removed and the sample is transferred to the top sieve of the nest of sieves. It is sieved, with the lid on, for two minutes. For this operation the second sieve is not used. The portion which passes through is again spread on an aluminium tray and exposed to the air of the room for four hours. 1.3 g. is then weighed into the tube with the aid of the scoop and aluminium funnel. Two such quantities are taken. The material in each tube is pressed down with a flat-ended glass rod to a height of 3 cm.

2. *Compressed Gun-cotton for Torpedo Warheads and Mines.* About 10 g. is removed from the centre of the primer or slab by scraping with a horn spatula. The scrapings are placed in a glass beaker of 1500 c.c. capacity, two-thirds full of distilled water, and stirred frequently for fifteen minutes. After settling, the water is poured off and replaced by the same quantity of water. It is again stirred for fifteen minutes, allowed to settle and decanted. The sample is collected by hand and the excess of water squeezed out. The wet gun-cotton is spread on six thicknesses of filter paper. Six other filter papers are laid on top and the sample is treated as described above for nitrocellulose pulp.

3. *Tonite and Analogous Nitrocellulose Preparations.* The sample is held over the rectangular sieve, and sufficient for the tests is scraped

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out from the centre of the cartridge with a horn spatula. The material is rubbed through the sieve by hand, and spread evenly on an aluminium tray. This is placed in the oven at 120° F. (48.9° C.) for fifteen minutes with the door closed. It is then removed and the sample transferred to the top sieve of the nest of sieves. It is sieved for two minutes with the lid on. For this operation the second sieve is not to be used. The sieved material is again spread on an aluminium tray, and exposed to the air of the room for four hours. 1.3 g. is weighed out on a scoop and transferred by an aluminium funnel to a heat-test tube. Two such quantities are spread out. The material is gently pressed down with a flat-ended glass rod to a height of 3 cm.

4. *Nitrocellulose Propellants.* (a) Explosives in the form of sticks or tubes: the procedure as for cordite in sticks or tubes is followed. (b) Explosive in the form of grains for small arms. A quantity sufficient for the tests is spread evenly on an aluminium tray. This is placed in the oven at 120° F. (48.9° C.) for fifteen minutes with the door closed. It is then removed and exposed to the air of the room for four hours. Three quantities of 1.3 g. each are weighed out with

a scoop, transferred by an aluminium funnel to heat-test tubes, and shaken down by tapping the tubes with the fingers.

5. *Ammonite, Bellite, Roburite, etc.* The contents of the cartridge are loosened. The first half inch is rejected, and 1.3 g. loosened into the scoop and transferred by means of an aluminium funnel to a heat-test tube.

C. Explosives of Class 4, Chlorate Mixtures, Divisions 1 and 2

These are treated as under Class 3 (p. 74).

Application of the Test. The heating bath is filled with water up to the outflow. It is placed in a north light in such a position that the papers can be observed by reflected light. The temperatures for the test with various explosives are given below.

The glass rod with platinum hook is inserted in the rubber stopper. A test paper is then held with forceps and pierced near the top with a needle. A small quantity of a mixture of equal volumes of glycerine and water is applied to the upper edge of the paper by means of the glass rod of the dropping bottle, so that it will moisten the upper half of the paper by the time the test is complete. The wetting of the paper requires considerable practice to ensure uniformity. The paper is then affixed to the platinum hook. At no time should the paper be touched with the fingers. The rubber stopper carrying the test-paper is inserted in the test tube containing the explosive, so that the bottom of the stopper coincides with the top line etched on the tube, and the position of the glass rod is adjusted so that the lower

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edge of the wet portion of the test paper coincides with the middle etched line on the test tube. The lower edge of the wet portion should be approximately horizontal. The test tube is then inserted in one of the holes of the bath so that the bottom line etched on the tube coincides with the lid of the bath. The tube should be fitted with a rubber ring flush with the lid of the bath. The cap is placed over the tube. The cap is lifted at intervals to observe the test paper, but should not be lifted unnecessarily. The test is completed when the faint brown line which appears on the paper becomes equal in depth of tint to the standard tint. The time is measured from the introduction of the tube into the bath, to the production of a tint equal to the standard tint. The following table summarises the limits for the different explosives:—

Abel Heat Test: Quantities, Temperatures and Time Limits

	Temperature.		Quantity.	Time Limit. Minutes.
	Degree F.	Degree C.		
<i>Class 3, Division 1.</i>				
Nitroglycerine extracted from dynamite, etc.	160	71.1	2 c.c.	15
Carbonite, Monobel and similar explosives from which the nitroglycerine cannot conveniently be extracted by water	160	71.1	3.2 g.	7
Blasting gelatine, gelatine dynamite and analogous preparations	160	71.1	3.2 g. + 6.5 g. French chalk	10
Cordite,* ballistite and other propellants of Class 3, Division 1	160	71.1	3.2 g.	10
<i>Class 3, Division 2.</i>				
Nitrocellulose pulp, compressed gun-cotton, tonite and analogous compressed nitrocellulose preparations	170	76.7	1.3 g.	10
Nitrocellulose propellants	170	76.7	1.3 g.	10
Ammonite, bellite, roburite, and analogous preparations	170	76.7	1.3 g.	10
* For the acceptance of New Cordite and Cordite MD for the British Naval and Military Services the details are as follows:—				
Cordite and Cordite MD	180	82.2	1.6 g.	30

Mechanism of the Abel Heat Test. The test depends upon the

liberation of iodine from the potassium iodide by nitric peroxide. The quantity of nitric peroxide necessary to colour the paper to the standard tint is very small. Robertson and Smart found it to be 0.000135 mg.

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The relation between the time of the test and the concentration of nitric peroxide was also studied by Robertson and Smart. A lag of about four minutes occurs at the start, due to the time of heating of the explosive. In some cases, however, the action on the test paper is not due wholly to decomposition during the test, but is in part due to nitric peroxide dissolved in the explosive.

The test has been frequently criticised on account of the minute quantity of nitric peroxide which is measured. This necessitates exact adherence to standard conditions of working in regard to the design of apparatus, preparation of the test-papers, etc. The exact end point is somewhat difficult to determine, and is liable to be affected by the illumination, notwithstanding the use of a standard tint for comparison.

In some cases the traces of decomposition measured may be due to relatively harmless impurities. The test may also be shortened by traces of oxidising substances, such as organic peroxides which liberate iodine from potassium iodide; on the other hand, the test may be masked by certain substances such as mercury.

The quantity of moisture present (in gun-cotton, for instance) may affect the results; if moisture condenses on the sides of the tube, nitric peroxide is absorbed. If, on the other hand, the test-paper becomes too dry, the sensitiveness is decreased.

According to Köhler and Marquoyrol calcium carbonate does not affect the test directly, but in presence of water it gives rise to hydrolysis of nitrocellulose and forms traces of calcium nitrite, which lower the test. If, however, the conditions be closely adhered to, it serves a useful purpose, especially in the manufacture of nitric esters. It is also very simple to apply.

Attempts were made at an early date to overcome the masking of the test by the use of other indicators in place of potassium iodide and starch. The zinc iodide test is, of course, open to the same criticisms.

(b) Zinc Iodide Test

This is a German modification of the heat test. Zinc iodide is used in place of potassium iodide. This renders the test rather more sensitive.

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(c) Guttman's Test

Guttman used a solution of diphenylamine in sulphuric acid as indicator to overcome the masking effect of mercuric chloride, etc., on the Abel test. Jannopoulos described a modification in which the finely ground powder is previously warmed to 35-38° for four days before testing. The tests are inapplicable to nitroglycerine powders, as the nitroglycerine vapour is decomposed by the sulphuric acid.

(d) Hoitsema's Test

Diphenylamine was also used in this test, but was applied on glass wool instead of paper.

(e) Spica's Test

In this test a solution of metaphenylenediamine hydrochloride was used. This is unduly sensitive and the indicator has poor keeping properties.

Various other reagents, such as indol, sulphanilic acid and alpha-naphthylamine, dimethylaniline, beta-naphtholsulphonic acid, etc., have also been tried as indicators.

(f) Hess Test

In this test the explosive was heated at 70° in a current of air, which was passed into a solution of zinc iodide and starch. The

time taken to impart a blue colour to the solution was noted.

(g) Vieille Test

In this test the decomposition is carried considerably further. Ten g. of the explosive is weighed into a glass tube, and a strip of litmus paper is placed in the upper part of the tube. The tube is corked and placed in a water-jacketed oven, the jacket being maintained at 110° . The actual temperature of the explosive is approximately 108.5° . If the litmus turns colour within ten hours, the tube is at once removed; otherwise the tube is removed after ten hours. In either case the explosive is exposed to the air overnight, and on the following day it is reheated similarly with a fresh strip of litmus. This is repeated every day until the colour-change occurs within

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an hour. The total number of hours of heating is then taken as a measure of the stability. The following limits are given by A. P. Sy. For large powders thirty hours; for small powders twenty hours; for ungelatinised nitrocellulose ten hours.

(h) Horn-Seifert Test

In the original test of Horn, 2 g. of powder was heated in a long test tube at 120° , and nitric peroxide was observed by looking down the length of the tube. A disc of white porcelain was laid on the surface of the powder to facilitate the observation. Seifert modified the test by introducing a test-paper (methyl-violet and rosaniline) and observing the successive changes of colour.

(i) Continuous Stability Test

The case in which the explosive was stored was fitted with a narrow metal tube communicating with a glass tube containing a porous material impregnated with litmus or other indicator. The gases evolved by the explosive on storage reacted with the indicator.

(j) Methyl Violet Test

Methyl violet is gradually turned blue green, and ultimately a pale salmon colour by nitric peroxide. It is much less sensitive than starch iodide. For the test, 2.5 g. of the dried sample of explosive is placed in a glass tube 29 cm. long and 1.5 cm. internal diameter. The sample is pressed down to occupy a depth of 5 cm. and a methyl violet paper is placed in the tube with its lower edge 2.5 cm. above the explosive. The tube is inserted in a bath at 134° to 135° so that about 6 to 7 mm. of the tube projects from the bath. After twenty minutes the tube is partially withdrawn to examine the paper, and this is repeated at intervals of five minutes until the paper becomes salmon-pink. The time of the test should be at least thirty minutes. The papers are prepared by dipping Schleicher and Schüll's filter paper No. 597 in a solution of pure rosaniline acetate (prepared from 0.25 g. basic rosaniline), 0.168 g. methyl violet (crystal violet), 4 c.c. glycerine, 30 c.c. water, made up to 100 c.c. with pure 95 per cent. alcohol. The dried paper is cut into strips 2×7 cm.

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(k) Pollard's Test

This depends upon the action of nitric peroxide on colloidal silver oxide. A current of air is passed over the powder and into a colloidal solution of silver oxide. The nitric peroxide reacts with the silver oxide and decreases the amount of light diffused by the colloid. The decrease forms a measure of the decomposition of the nitric esters.

(l) Jensen's Test

Nitrocellulose powder is heated gradually from 100° upwards as in the deflagration test. A strip of iodide paper is suspended over the powder and the temperature at which the test-paper gives a coloration is taken as an indication of the stability of the powder.

II. STABILITY TESTS DEPENDING ON THE DIRECT OBSERVATION

OF BROWN FUMES

(a) Simon Thomas Test (1898)

The explosive is heated at 100° for eight hours each day until visible fumes appear. The test has subsequently been used in Holland in a slightly altered form. A quantity (usually $2\frac{1}{2}$ g.) of explosive is heated to 95° , first for four hours in an unstoppered flask, and then for eight-hourly periods. In general nitrocellulose requires fourteen to twenty-four daily periods. The test is stated to give good results for ungelatinised nitrocellulose, but to be less satisfactory for propellants.

(b) American Test at 65.5° or 80°

A hard glass-stoppered bottle of 8 oz. capacity is filled to one-third with the propellant and maintained at 65.5° or 80° until brown fumes appear. The time of the test ranges up to 300-400 days at 65.5° or 75-100 days at 80° . As the powder deteriorates, the time of the test decreases until ultimately tests of one to six days are obtained.

(c) International 75° Test

Two samples of 10 g. each are placed in capsules 35 mm. diameter and 50 mm. in height; the capsules are loosely covered with watch glasses, and are heated for forty-eight hours at 75° . The appearance and odour of the powder and the formation of nitrous fumes are

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noted. If there is any positive indication of decomposition the explosive is considered to be of unsatisfactory stability.

(d) Warmlagermethode 75°

This test is largely used in Germany for nitrocellulose and propellants. Five g. of the explosive is heated in stoppered tubes of 200 mm. length and 28 mm. diameter at 75° . The tubes are left open for sixteen hours and are then stoppered, and the heating is continued without interruption until distinct brown fumes appear. They are opened once a week for ten minutes to renew the supply of oxygen necessary to convert NO to NO_2 . The test is stated to give reliable results and to give good concordance in tests done on the same powder at different times. A temperature of 100° is sometimes used.

III. STABILITY TESTS DEPENDING ON SPONTANEOUS HEATING OF THE EXPLOSIVE

(a) Silvered Vessel Test

This test was devised by Robertson for the testing of cordite. The apparatus consists of a vacuum-jacketed flask, which is maintained at 80° in a bath. The cordite is ground as for the heat-test, and 50 g. is placed in the flask. A thermometer is fitted in the neck of the flask with its bulb in the ground cordite. The neck of the flask has a lateral side-tube for the observation of brown fumes of nitric peroxide. The test is continued until the thermometer shows a rise of 2° due to spontaneous heating of the cordite. The time is then noted, and taken as a measure of the stability. The test usually requires several hundred hours, but the time varies greatly with the nature of the powder.

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(b) Taylor's Test

In this test 4.5 g. of nitrocellulose is heated in a tube 30 cm. long and 1.4 cm. in diameter at 135° . A thermometer is fixed with its bulb embedded in the nitrocellulose, and the heating is continued until a rise of temperature is indicated. This usually requires forty-five to sixty minutes.

IV. TESTS IN WHICH DECOMPOSITION IS CARRIED TO EXPLOSION

(a) German 132° Test

This test has been used to a considerable extent in Germany for the testing of nitrocellulose and powders. The nitrocellulose is dried and heated in a glass tube. Observations are made of the change of colour of litmus paper, the formation of brown fumes and the explosion of the samples. The test was formerly carried out at 135° , but is now carried out at 132° and the observations are frequently confined to the brown fumes. For the test as formerly carried out the following limits were given by Sy.

	Litmus.	Fumes.	Explosion.
Ungelatinised nitrocellulose	30 mins.	45 mins.	5 hrs.
Nitrocellulose powder	75 "	120 "	5 "
Nitroglycerine powder	30 "	45 "	5 "

In the test as now carried out, 2.5 g. of the sample of nitrocellulose or smokeless powder is placed in a tube 350 mm. long, 16 mm. internal diameter, and 19 mm. outer diameter. A strip of blue litmus is pushed down so that it is 25 mm. above the explosive. The glass tube is loosely closed with a cork disc or a paraffined cork, and put into a bath containing boiling xylene, with a reflux condenser. The cover of the bath is provided with orifices to hold the tubes. The orifices are 11 cm. deep and contain glycerine.

Uniformity of the litmus is of great importance.

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(b) Deflagration Test

A bath of mineral jelly is heated to 100° . Test tubes, each containing 0.1 g. of explosive, are suspended in the bath, and the temperature is then raised at the rate of 5° per minute. Little paper caps are lightly fixed on the mouths of the tubes to indicate which sample has exploded. The temperatures of explosion are noted. Berl and Rueff described an apparatus consisting of a copper block, heated electrically, with holes for the test tubes.

A combination of the deflagration test with the Abel test is given by Jensen.

(c) Time to Explosion

In some cases the explosive is maintained at constant temperature, and the time to explosion is measured. Patterson gives a number of results, of which the following is an example:—

Temperature	136°	139.5°	143°	148°	160°	168°
Time to explosion	5 hrs.	2 hrs.	1 hr.	30 m.	16 m.	12 m.

Weber describes an apparatus in which the powder is heated in glass tubes at 160° , 170° , 180° and 200° and the time to explosion is measured.

V. QUANTITATIVE DETERMINATION OF NITRIC PEROXIDE

Bergmann and Junk Test

This test is widely used for the testing of nitrocellulose. The apparatus is shown in Fig. 6. The heating tube consists of a glass tube, 35 cm. long and 19 mm. in diameter. The ground glass neck is fitted with an absorption vessel containing water. The nitrocellulose is well dried and 2 g. is placed in the tube, which is then heated in a bath of special construction. The bath is maintained at 132° by a boiling liquid. After two hours' heating the tube is removed from the bath, and water is poured into the cup. As the tube cools, the water is drawn into the main tube. The cup is rinsed out with water into the main tube, the volume being made up to 50 c.c. The tube is

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well shaken and the contents filtered. A little permanganate is added to oxidise nitrous acid, and the nitrogen is estimated by the Schulze-Tiemann method. Titration with alkali has also been used to determine the nitrous and nitric acid, but in this case allowance must be made for the calcium carbonate in the nitrocellulose.

The test has generally been found very reliable. Sometimes rapid decomposition sets in and the test has to be discontinued; occasionally explosions occur. For this reason a modified test has been devised

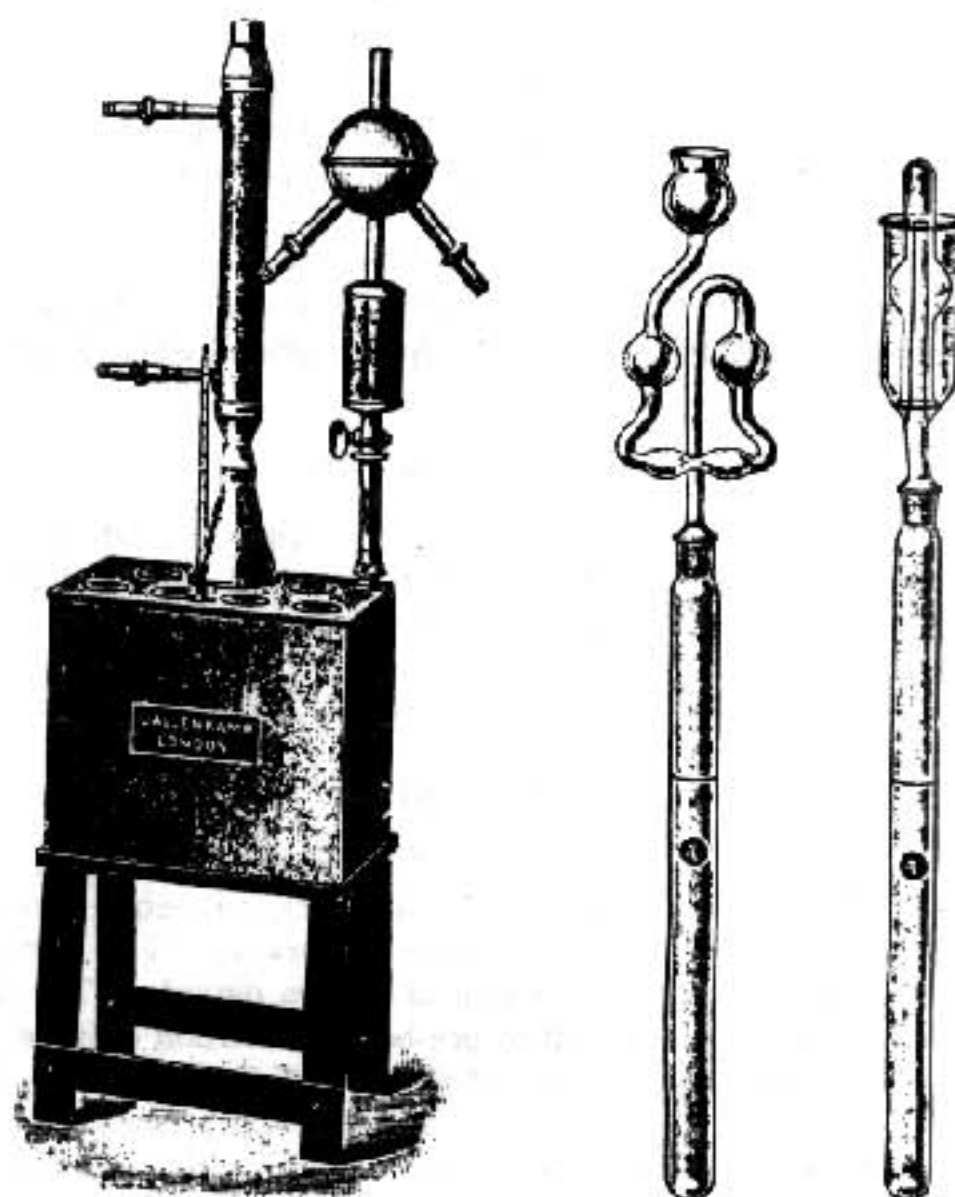


FIG. 6.

by V. Meerscheidt-Hüllessem in which the reaction tube can be rapidly cooled without removing it from the bath.

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A modification of the test is described by Mayrhofer. In this the nitric peroxide is collected in potassium iodide solution, which is then titrated with thiosulphate. A special feature of the modified method is the addition of 0.05 to 0.25 c.c. of water to the 2 g. of explosive, to facilitate hydrolysis of the esters. Comparative tests are carried out under the wet and dry conditions. The method is stated to be applicable to nitroglycerine powders.

The Bergmann and Junk test is applied to nitrocellulose powders in Germany. Five g. of powder is taken for the test, and parallel tests are made on a control powder. A good nitrocellulose powder with stabiliser is stated to give 5 to 8 c.c. of nitric oxide after five hours' heating.

VI. LOSS OF WEIGHT DUE TO DECOMPOSITION

(a) Method of Sy

The unground powder is heated at 115° on an open dish for eight hours daily for six days. The daily loss of weight is determined. Limits are given for nitrocellulose powders of different thicknesses. The test has been criticised on the ground that the volatile catalysts do not exert their due influence, and further, that different powders in the same oven may affect one another.

(b) Method of Meerscheidt-Hüllessem

In this test 10 g. of the unground powder is heated in a glass tube to retain the volatile catalysts. The tubes are 200 mm. long and 30 mm. in diameter and are maintained for eight hours each day at 115° in a bath capable of holding a large number of tubes. The samples are weighed every day up to about ten days.

(c) Dutch Test

Thomas's original test (p. 80) has been gradually developed, and has taken the form of a "Loss of Weight" test. In this form it has

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received considerable attention in Holland for smokeless powders.

The apparatus consists of a glass tube 160 mm. long and 18 mm. internal diameter, with a glass stopper. Four g. of the powder, finely ground and passed through a 0.5 mm. sieve, is placed in the tube, which is then heated at 104° to 106° for nitroglycerine powders and 109° to 111° for nitrocellulose powders. The tube remains open for the first eight hours, but is closed during each subsequent heating. The sample is weighed every morning and evening. Stable powders should not lose more than 2 per cent. from eight to seventy-two hours.

(d) Brunswig's Test

Five g. of powder is heated in an open glass dish in an oven of special construction fitted with a revolving stand. The loss of weight is determined, first after three days' continuous heating at 110°, and then after daily periods of eight hours.

VII. GASOMETRIC STABILITY TESTS

(a) Will Test

This is used as a rule only for ungelatinised nitro-cotton. It is a valuable test for the control of the manufacture, but requires considerable attention and somewhat elaborate apparatus. The nitro-cotton (2.5 g.) is heated at 135° in a current of carbon dioxide. The heating tube is fitted with a glass spiral to pre-heat the carbon dioxide, before it reaches the explosive. The oxides of nitrogen evolved by the explosive are carried forward by the carbon dioxide, passing through a copper U-tube containing copper and copper oxide, which is maintained at a red heat. All oxides of nitrogen are thus reduced to nitrogen, whilst carbon monoxide and hydrogen are converted to carbon dioxide and water. The gases are then led into a gas-measuring tube filled with potassium hydroxide solution. This absorbs the carbon dioxide, and leaves the nitrogen, which is measured at intervals of fifteen minutes for four hours. The heating tubes are enclosed in a metal case with strong glass windows, as explosions occur occasionally. A good nitro-cotton gives a uniform evolution of gas, whilst unstable nitro-cottons give an irregular and increased evolution. Purity of the

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carbon dioxide is of importance.

A modification of the test has been described by Goujon in which the heating tube is enlarged to hold 10 g. of nitro-cotton. The quantity of nitrocellulose is reduced to 0.3-0.5 g. An electrically heated copper block is used in place of a liquid bath.

As all volatile substances are driven off by the current of gas, the Will test measures essentially the decomposition due to non-volatile catalysts such as traces of sulphuric acid.

(b) Dupré's Vacuum Test

One g. of the ground dried powder is placed in the test tube. The top of the tube ends in a flat ground surface, and the joint is made between this and a similar flat surface of the connecting tube by means of luting composition. A similar joint is made to the manometer which consists of a syphon barometer. The bath is kept at a constant temperature, e.g. 125°, by boiling water under increased pressure. The evacuated tube is placed in an orifice in the bath. After half an hour the tube is re-evacuated and the test started five minutes later. Readings of the manometer are then taken every half-hour for about four hours. The tubes can be re-evacuated if necessary.

(c) Mittasch's Method

The chief feature of this test is that the rise in pressure of the gases is registered automatically. This necessitates more complicated apparatus, and the practical application of the test has been very limited.

(d) Obermüller's Method

In this test the explosive is heated in a vacuum, and the gas evolved is measured by means of a mercury manometer. Various forms of

the test have been described. In one of these 1 to 2 g. of nitro-cotton are placed in a tube of 12 c.c. capacity which is heated at 135° or 140°. A small glass rod rests on the nitro-cotton to prevent it from being ejected upwards on application of the vacuum. Useful results have

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been obtained for ungelatinised nitro-cotton, but the test appears to be unreliable for gelatinised powders after storage. This is probably due to the continuous removal of the volatile catalysts.

(e) Brame's Method

This also depends on the measurement of the rise of pressure in an evacuated tube containing the explosive, by means of a mercury manometer.

(f) Chiaraviglio and Corbino

These authors describe a method in which a very sensitive manometer is used to measure the rate of decomposition at relatively low temperatures.

(g) Taliani's Test

This test has a device which prevents the volatile products from reaching the cool parts of the apparatus, thus ensuring that the catalysts are kept in contact with the explosive, and also preventing the distillation of nitroglycerine, when this forms a constituent of the explosive. The apparatus is shown in Fig. 7. The tube A containing 1.3 g. of the explosive is fitted with a tap C, and connected with a tube which has a double bend B. The U-shaped part of this tube is partly filled with heavy paraffin. This part of the apparatus is entirely enclosed in the hot bath. The tube B is further joined by a rubber connection to a glass tube leading to the manometer F. One limb of the manometer is divided into two tubes, one of which is fitted with a tap as shown. The paraffin trap prevents the volatile products from entering the manometer.

The test is usually carried out at 120° with nitroglycerine powders and 135° with nitrocellulose. The tap C and the manometer tap remain open until equilibrium has been obtained in the whole apparatus and any moisture has evaporated. When the taps are closed, any gases evolved from the explosive exert a pressure on the paraffin. By raising the mercury reservoir, the paraffin can be

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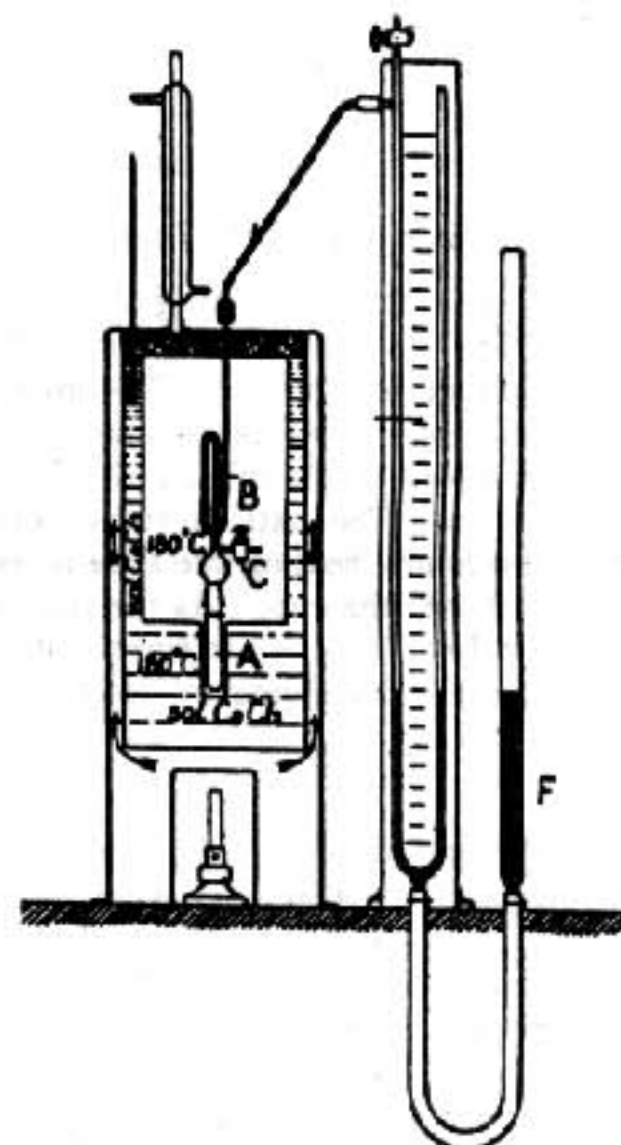


Fig. 7.

brought to the same level in the two limbs. The pressure is then read off on the scale. Readings are taken every five minutes until the difference of pressure reaches 100 mm. or 300 mm. Good drying of the explosive is necessary, as the results are affected by moisture. Calcium carbonate also has a marked effect.

(h) V. Meerscheldt-Hüllessem's Test

One of the main features of the test of Taliani described above is that the volatile products are not allowed to escape. This can also be effected by enclosing the powder in a vessel containing liquid paraffin with a syphon tube arranged so that the gases evolved displace the liquid and cause it to overflow into a beaker which can be periodically weighed. The test is carried out at 120° with measurements every fifteen or thirty minutes. The method is simple, but very few results have been published so far.

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(i) Desmaroux Test

A copper bath is filled with glycerine and maintained at constant temperature by a regulator. It is double walled to conserve the heat and has a number of orifices to receive the glass heating tubes. These are 3 cm. in diameter and 10 cm. high. Each tube has a ground glass stopper with a capillary outlet leading to a mercury manometer. Ten g. of explosive is placed in the tube, which is then evacuated. The tests are carried out at 75° and 108.5° and the rate of decomposition is measured by the rise of pressure in the manometer.

(j) Marquayrol's Test

The explosive is heated at 50° in a vacuum, and the slow evolution of gas is measured by means of a manometer. Readings are taken every three or four days over a long period.

VIII. MEASUREMENTS OF ACIDITY

One of the primary causes of instability of nitrocellulose and gelatinised explosives is the presence of traces of acidity, or of unstable esters which readily break down, yielding acids. Since esters are hydrolysed by moisture in presence of acids, the decomposition is autocatalytic, and the presence of acid is thus of great importance.

(a) Angell's Test

This is designed primarily for gelatinised powders. The powder is ground or cut into very thin flakes and 0.5 g. placed in a test tube. A small quantity of distilled water is added, and then 3 or 4 drops of a 0.2 per cent. alcoholic solution of dimethylaminoazobenzene. The whole is well mixed and either warmed for a few moments in boiling water or allowed to stand in the cold. The solid powder takes up the indicator and becomes more or less red according to its degree of acidity.

(b) Tomonari's Test

This test is applied to ungelatinised nitrocellulose. It depends on the solubility of acidic impurities of the nitrocellulose in methyl alcohol. One g. of the nitrocellulose is boiled for fifteen minutes with methyl alcohol and the solution is titrated with 0.01 *N* sodium

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hydroxide solution, using methyl red as indicator. The titre is called the acid number (x), and $100/x$ is called the *stability number*. The explosion temperature falls with a rise in the value of x . When x is less than 5 the cellulose nitrate is considered stable.

(c) Measurement of pH Value

This method depends upon extraction with water and measurement of the acidity either by indicator solutions or by the quinhydrone

electrode.

It is necessary to use pure water, as used for electric conductivity work, and to adhere to constant conditions of working. The method is frequently combined with a heating trial. Thus Hansen heated smokeless powders in the ground condition at 110° and tested samples at intervals of an hour by means of the quinhydrone electrode to ascertain the rate of formation of acid. In a modified method the powder is heated under water at 100° to bring about a hydrolytic decomposition. Grottanelli passes a slow current of air over a large sample (500 g.) of powder, which is maintained at 80°, and then into an absorption vessel in which the pH value is measured. Pavlik also passes the gases into water under modified conditions. The effect of calcium carbonate in powders has been examined by Metz.

(d) Conductivity Method

De Bruin and de Pauw have described a method depending on the electrolytic conductivity of an aqueous extract of the explosive. A number of flasks, each containing a weighed quantity of dried nitrocellulose or powder, are first heated to drive off residual moisture. The contents of one of the flasks are treated with 150 c.c. of "conductivity water," well shaken, and allowed to stand. The flask is again shaken, the liquid is filtered, and its conductivity measured. The other flasks are heated at constant temperature (100° to 132°) for known periods and the conductivity is similarly determined. The conductivity increases with the duration of the heating, and this increase is taken as a measure of the stability.

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IX. STABILITY OF HIGH EXPLOSIVES

The aromatic nitro-compounds, which form the basis of most of the high explosives used for Service purposes, do not as a rule respond readily to such tests as the Abel heat test. In general these compounds undergo very little deterioration on storage, but in some cases it is necessary to test them. The most reliable results of definite value in the comparison of high explosives are obtained by vacuum stability tests.

Vacuum Stability Test

The explosive is dried and weighed out into a test tube of the pattern shown in Fig. 8. The manometer is attached and the tube evacuated and placed in a thermostat of special design. The temperature of the test varies from 80° to 180° according to the explosive under test. The progress of the decomposition is followed by readings of the mercury manometer.

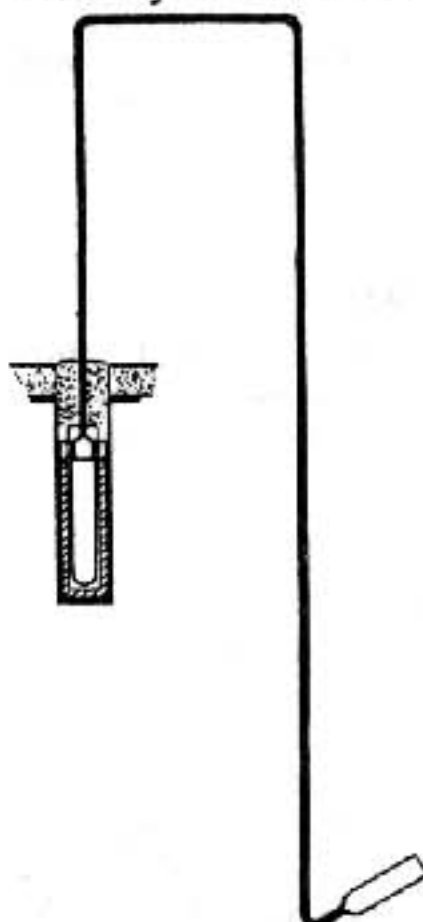


FIG. 8.

Method of Hald, Becker and Dittmar

The apparatus consists of a glass vessel connected with a manometer. The explosive is dried over phosphorus pentoxide, and 42 g. introduced through a side-tube which is then sealed off. The manometer is in the form of a U-tube and contains mercury covered with a layer of paraffin. The glass vessel is also fitted with a side-tap. It is heated in a bath to 75° and completely sealed. The evolution of gas is then measured by means of the manometer.

Acidity Measurements

The method of pH determination is applied as in VIII (c) above (p. 91). Five g. of explosive is heated at temperatures ranging from 75° to 132° according to the nature of the explosive, and the gradual fall of pH is measured by periodic tests.

Loss of Weight

In Germany, industrial blasting explosives are exposed to a temperature of 75°. Ten g. is heated in a loosely covered weighing bottle, 30 mm. diameter and 50 mm. high, and the loss of weight is determined periodically.

MATCHES AND FIREWORKS

A. MATCHES

I. NATURE OF MATERIAL FOR MATCH-STEMS

1. Woods

WHITE or soft pines of Canadian origin are largely used in the manufacture of matches. The pine tree grows to a height of 100 ft. or more, and is 7 ft. or more in diameter. For the manufacture of matches the young pine, on account of its very soft texture, is to be preferred. It is essential to have the wood dry and thoroughly seasoned, thereby reducing the water content and improving its physical properties by rendering it less brittle. The wood should be stored in well-ventilated sheds and protected from the sun and rain.

In addition to pine, fir and spruce, the following woods are used, especially in countries to which these are indigenous, viz.: aspen, poplar, lime, beech and willow, and to a more limited extent, alder-wood. Aspen wood, which comes mainly from Russia, is very easy to flake and gives splints of uniform size. The strips of wood for match boxes are also made from the aspen tree and on the same machine. It is probable that for match splints aspen wood will supplant pine wood in this country.

Fir woods closely resemble the pines in being needleleaf or soft woods but have no resin ducts. The variety mostly favoured is the white or silver fir.

Spruce woods resemble the soft pines. They grow extensively in North America and Europe. The common varieties are the Norway spruce (*Picea excelsa*) and the Douglas spruce or fir (*Pseudotsuga douglasii*). The Norway spruce resembles silver fir but the resin ducts are visible though few in number.

2. Wax Matches or Vestas

The stems of wax matches consists of a wick of twisted cotton threads, coated with wax, or more generally with mixtures of stearin, paraffin, and gum dammar or gum opal. These matches burn for a longer time than matches made from wood.

3. Cardboard Matches

Within recent years safety-matches with stiff paper or cardboard stems have become very popular, and numerous patents have been taken out for the manufacture of such matches, e.g. B.P. 288620/1927 and B.P. 332700/1929. These are usually made up in the form of a book, and generally consist of two rows of ten matches each in a cover. These matches are made automatically by machinery. The cardboard is slit and dipped, and the composition then put on the cover. The machine also binds and cuts the books apart. Matches are also produced in disc form and in the form of a cylinder. When a match is withdrawn from the latter bundle it is ignited by friction. Various details of paper matches are described in U.S.P. 2,022,088 (1936). Hand dipping in batches still survives to some extent in cardboard match manufacture.

II. SUBSTANCES USED TO IMPREGNATE THE SPLINTS

The match sticks are either square or round, according to whether they are made by flaking or planing. The grooved splints, sometimes employed, are punched by upward cutting dies from small wooden

blocks fed into the machine in a special way. The round splints are compressed, and have a closer texture than the square sticks, and are better suited for sulphur-coated match manufacture. The sulphur which coats the lighting end does not enter the pores, so that a loose structure is unnecessary. With the majority of other dipping substances it is preferable to have a porous foundation, as the substances tend to penetrate the wood. Sulphur is now scarcely ever used. Paraffin and other waxes are generally employed to impregnate the splints. In addition resin and other fatty acids such as stearic are commonly employed. These will be considered individually. To prevent the after-glow of the splints, and the falling-off of the glowing ember, the splints are dipped into a solution of phosphoric acid and ammonium nitrate, or other fire-proofing materials, such as alum or boric acid. Hygroscopic substances should be avoided.

A solution of celluloid in amyl acetate may be used in place of gum, etc., as binder in order to render the match damp-proof. The stems and heads may be dipped in a similar solution. A moisture-proof match-ignition composition containing cellulose derivatives has also been suggested in other patents (e.g. 355901/1930).

1. Paraffin and Other Waxes

Waxes, which are usually the fatty esters of the monohydric alcohols, find a limited application in the match industry. Paraffin wax, a

hydrocarbon, is the most important in this connection. It is the highest boiling fraction of the products of distillation of paraffin and lignite. It is sold in different grades according to its melting point, which may range from 35° to 60° C. For the manufacture of matches the more or less yellow and brown, soft, scaly variety is the most important. Paraffin waxes with a melting point of 98° to 102° F. (Scotch method), 101° to 105° F. (American method), and 38° to 39° C. (German method) are the most favoured.

The determination of the melting point of wax may be carried out as follows: 0.5 g. is weighed approximately (first time, afterwards judged by size) and wedged at the top of a hook of platinum wire (0.025 in. diam.) fused on to the end of a glass rod, which passes through a hole in the cork fitted into a dry test-tube. The cork also carries a thermometer with its bulb near the platinum hook. The test tube is slowly heated in water and the melting point noted. Alternatively, the wax may be melted in a small beaker, slowly stirred with a thermometer, until the temperature becomes steady for a short period, with solidification of the mass. For more accurate determination a large bath is employed and the liquid mechanically stirred. When the melting point is not sharp and for petroleum jellies the apparatus of Ubbelohde may be employed. A small quantity of the jelly is pressed into a small glass perforated cup which fits on to the bulb of the thermometer. On slowly heating, the temperature at which the drops of liquefied paraffin fall away from the cup is noted. The English method of determining the setting point of paraffin wax consists in filling a test tube (1 in. diam.) to a depth of 2 in. with molten paraffin and inserting a small accurate thermometer. The tube is then allowed to cool and the temperature at which the thermometer remains stationary for a short period is regarded as the setting point.

Shukoff's apparatus for determining the titer test of fatty acids consists of a tube 3 cm. diam. surrounded by a Dewar vacuum mantle, the outer diameter of which is 5 cm. and the height 10 cm. The molten paraffin is poured into the inner tube, which is closed by a cork fitted with an accurate thermometer. The vessel is slowly cooled with shaking and the point at which without further shaking the thermometer remains steady and then rises is noted. The highest point is taken as the setting point.

Considerable uncertainty still exists as to the manner in which the English, Scotch, American and German methods of examination are carried out. The German and American methods are in close agreement when Fahrenheit degrees are converted into Centigrade degrees

by the well-known formula $C^{\circ} = (F^{\circ} - 32) \times \frac{5}{9}$; whereas after convert-

ing the English or Scotch degrees by the same formula, it is always necessary to add on 2° C. Ignorance of this difference in the methods is often taken advantage of by dealers, as paraffin wax is sold according to melting point, and the German test gives higher results.

The wax commonly used when first obtained is yellow; if melted and poured into cold water, it forms thin strips which are bleached white by the action of the air. In this country, wax for the manufacture of wax matches has been partly or entirely replaced by stearin with or without paraffin wax. Cotton threads or bobbins are passed through a ring so as to form one single thread, which is then passed through a trough containing the molten wax mixture. This thread is then passed through a wire-drawing plate which gives it an exactly cylindrical shape and a smooth surface. The wax mixture used usually contains about 10 to 15 per cent. of paraffin wax. Wax matches for tropical countries contain a small amount of Carnauba wax. The latter is a hard vegetable wax which raises the melting point and increases the hardness of the wax, thus preventing the matches from sticking together.

In impregnating the splints with paraffin wax the molten paraffin is heated to such a point that a match stick "boils" when plunged into it. As the vapour of paraffin wax is unpleasant, it is desirable to fit an efficient air draught to the paraffin bath.

2. Stearin (Stearic Acid)

Stearic acid, incorrectly called stearin, is one of the higher fatty acids. It is a waxy, crystalline solid, which melts at 69.2° . It is made on an industrial scale from animal and vegetable fats. These are hydrolysed by means of superheated steam alone or with addition of a small percentage of calcium hydroxide. The calcium salt produced is changed into stearic acid by the addition of the requisite amount of sulphuric acid.

Stearin was used, at one time, with the addition of a little resin, in the preparation of the wood for matches "de luxe." In the manufacture of matches it is unnecessary to use the hardest and whitest sorts of stearin, as the softer kinds have been found to give even better results. Stearin has been replaced by paraffin for making wood matches, but it is still used, with gum opal or dammar, for wax match stems. In the match industry the only test required is to determine the melting point of the stearin before use. In this connection the Shukoff method for determining the melting point of paraffin wax (*cf.* p. 96) is used.

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3. Resin

The dried resin of the coniferae is used in match compositions, or for mixing with the stearin; Venice turpentine is the best. Addition of resin causes the flame to smoke strongly. The addition of insoluble synthetic resins as binding material is claimed to give a match-head unaffected by water.

4. Sulphur

For occurrence, examination for purity, etc., see Vol. I., pp. 358 *et seq.*

Sulphur melts at 114.5° C. to a clear yellow liquid, which, on further heating to above 125° C., becomes darker and very viscid; at 400° C. it is again yellow and mobile and begins to volatilise. During cooling these phenomena reappear in inverse order. If the sulphur becomes thick, it is too hot, and must be cooled further before the splints can be dipped.

For the manufacture of matches very pure sulphur is not needed. The small amount adhering to the splint always appears pure and is inflammable. Finely powdered roll-sulphur is preferred to flowers of sulphur for the manufacture of safety-match compositions.

Differences between Powdered Sulphur and Flowers of Sulphur under the Microscope. The powdered sulphur consists of more or less transparent crystals, while flowers of sulphur consist of dark, cauliflower-shaped masses. In polarised light, between crossed nicols, flowers of sulphur are devoid of optical activity, while the crystalline

particles of the powdered sulphur appear light on a dark ground. Sulphur is scarcely ever used as a coating for match splints in this country, although it is an essential ingredient of some match compositions, especially those used for safety-matches.

III. MATERIALS FOR MATCH COMPOSITIONS

A. COMBUSTIBLE SUBSTANCES

1. **Ordinary or Yellow Phosphorus.** — Phosphorus is usually prepared from bones or naturally occurring phosphorite, in both of which it is present as tricalcium phosphate. At ordinary temperatures yellow phosphorus is a crystalline solid having a sp. gr. of 1.83 at 10° . Above 15° it becomes soft and waxy, melting at 44.4° to a yellow liquid. It is readily soluble in carbon disulphide, chloroform, benzene and sulphur chloride (S_2Cl_2), and almost insoluble in alcohol and water. Friction, or warming to 60° , in the air causes phosphorus to burn with a bright, yellowish white flame, to phosphorus pentoxide,

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P_2O_5 . Yellow phosphorus is a deadly poison, as little as 0.1 to 0.2 g. causing death; inhalation of the "fume" causes "phossy jaw," or necrosis of the jaw-bone, a disease prevalent amongst workers in the match factories. Fortunately, its use in most countries is now prohibited by law.

Examination of Commercial Yellow Phosphorus. The impurities present in yellow phosphorus are traceable to the sulphuric acid used in its manufacture. The principal adulterants are sulphur, arsenic and iron. To test for sulphur, a fragment of the phosphorus is dissolved in dilute nitric acid, and the solution, which now contains the phosphorus as phosphoric acid, is tested with a solution of barium nitrate; a white precipitate, insoluble in nitric acid, indicates the presence of sulphur in the phosphorus. Another portion of the solution is diluted, nearly neutralised with alkali, and treated with sulphuretted hydrogen; any arsenic originally present exists as arsenic acid in the nitric acid solution. The latter with hydrogen sulphide gives a yellow precipitate of arsenious sulphide. If iron is present, a precipitate of Prussian blue is obtained, on the addition of a few drops of potassium ferrocyanide solution to the nitric acid solution.

2. **Dark Red Phosphorus**, a second allotropic form of phosphorus, is manufactured on the large scale by heating the yellow variety in sealed iron cylinders for a few minutes at 250° to 300° . Red phosphorus differs considerably in properties from the yellow form. It is non-poisonous, is unaffected by the air and is insoluble in carbon disulphide. Moreover, it is odourless. It has a sp. gr. of 2.106. When heated in air it does not ignite until a temperature of 200° is reached. Generally it is less chemically active than yellow phosphorus.

Red phosphorus is used chiefly for the preparation of the striking surfaces on safety-match boxes and is also occasionally employed in the manufacture of "strike anywhere" match compositions. While pure red phosphorus is non-poisonous, the commercial product can act as a poison, as it frequently contains traces of the white modification. Fresenius and Luck analysed a sample of commercial red amorphous phosphorus with the following results:—

Red phosphorus	92.630 per cent.
White phosphorus	0.560 "
Phosphorous acid	1.302 "
Phosphoric acid	0.880 "
Water and impurities	4.662 "

Although the presence of a small amount of white phosphorus is not in itself detrimental in match-making, it has been assumed to be

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the cause of a slow oxidation to phosphorous and phosphoric acids, which on account of their acid and hygroscopic properties, act on the other substances present. This supposition is, however, unnecessary, for red phosphorus, which has been carefully purified, becomes

oxidised after long contact with air, and contains under these circumstances considerable quantities of phosphorous acids. Factories do not generally trouble about any special examination or purification, although in 1909 it was proposed to use "neutral amorphous phosphorus" obtained from the ordinary product by purification methods. The phosphorous acids are estimated quantitatively by extracting a weighed quantity (10 g.) on a filter with warm water, until the filtrate no longer reacts acid. A definite portion of the filtrate is now oxidised by repeated evaporation with nitric acid, and the total phosphoric acid then precipitated with magnesia mixture.

The phosphorous acid is estimated with mercuric chloride in another portion of the filtrate. To estimate the percentages of white and red phosphorus present, Fresenius and Luck (*loc. cit.*) oxidise the phosphorus, after washing free from acids with warm water, with fuming nitric acid to phosphoric acid, and estimate the amount of phosphorus in this as magnesium ammonium phosphate. The quantity of red phosphorus is similarly estimated in another portion of the sample, after extracting the yellow variety with carbon bisulphide. The difference between these two quantities gives the amount of white phosphorus present.

The German official method, worked out by Siemens, is as follows:—Three g. of phosphorus is dried, and boiled for half an hour on a steam-bath, under a reflux condenser, with 150 c.c. of benzene, and filtered. One c.c. of this solution is added to 1 c.c. of a solution of ammoniacal silver nitrate, made up by dissolving 1.7 g. of silver nitrate in 100 c.c. of ammonia of sp. gr. 0.922. If, after shaking and allowing to stand, no change or only a yellow coloration of the aqueous solution takes place, white phosphorus is absent. But if the aqueous solution is coloured red or brown or contains a black or brownish-black precipitate, white phosphorus is present. The colour of the aqueous solution should be judged directly after shaking and allowing to stand, and not after prolonged standing.

3. Light Red Amorphous Phosphorus, sometimes called scarlet phosphorus, is another allotropic form. It is prepared by dissolving yellow phosphorus in phosphorus tribromide and boiling the solution. The new modification separates out of the solution as a finely divided, amorphous powder. Like dark red phosphorus, the scarlet form is not poisonous. It is, however, more chemically reactive than the former owing to its more finely divided condition. Conversion of scarlet into dark red phosphorus may be brought about by continued

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heating at 300° in a current of carbon dioxide. Schenck determines the phosphorus by heating a weighed quantity with water, together with bromine contained in a small tube, in a sealed tube, for two or three hours in a steam-bath at 100°; the oxidised phosphorus is weighed as magnesium pyrophosphate.

Scarlet phosphorus is used in compositions for parlour matches, *i.e.* matches requiring no special ignition surface.

4. Phosphorus Sesquisulphide (P_2S_5).—This compound is formed by slowly heating the calculated quantities of phosphorus and sulphur in a current of carbon dioxide at 330°; a small excess of sulphur is used. By sublimation at 260°, regular crystals are obtained, but on crystallisation from carbon disulphide, rhombic prisms melting at 166° and boiling at 380° are obtained. Phosphorus sesquisulphide is soluble in carbon disulphide, phosphorus trichloride and in aqueous solutions of sodium and potassium sulphides. Alkalis readily decompose it. The commercial product ignites in air at 98° to 99°. Cold water has no appreciable action on phosphorus sesquisulphide, but boiling water decomposes it into sulphuretted hydrogen and phosphorous acid. The commercial product sometimes contains free phosphorus, the presence of which is detected by passing a current of hydrogen over the sulphide when, if phosphorus is present, the issuing gas will burn with a green flame. The pure product keeps well in stoppered bottles, but the commercial product gradually decomposes with evolution of sulphuretted hydrogen.

Phosphorus sesquisulphide was officially introduced into France by Sevéne and Cahen for the manufacture of "strike anywhere"

matches, free from white phosphorus. It is now used in the manufacture of matches almost to the exclusion of yellow phosphorus.

The examination of phosphorus sesquisulphide is carried out first, by the smell (odour of phosphorus) and then by Mitscherlich's test (*cf.* detection of phosphorus in match-heads, p. 134), or by the method of Schenck and Scharff. These methods are exact and permit the detection of very small traces.

5. Lead Thiosulphate (PbS_2O_3) is now used for the preparation of match compositions, which ignite on any surface. It is prepared by treating a solution of "sugar of lead" (lead acetate) with sodium thiosulphate; it is a pure white, inodorous, tasteless powder, insoluble in water and not hygroscopic. It should be kept in well-closed bottles. Twelve kg. of lead acetate yield, when treated with 5 kg. of sodium thiosulphate, about 9.5 kg. of lead thiosulphate. A pure sample should contain no water-soluble matter.

6. Antimony Trisulphide (Sb_2S_3) is used to some extent for match compositions, but principally in the preparation of the striking surface

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of safety-match boxes. It can be obtained in a purity of 99 per cent. Tests for purity are not necessary.

7. Other Substances.—A few other substances have been recommended for match compositions, such as persulphocyanic acid, ferrocyanogen compounds, potassium xanthate, thiocyanates, "sulphocuprobaryum polythionate" and "thiophosphit." Thiophosphites made by heating such sulphides as antimony and zinc sulphides with red phosphorus and sulphur in an atmosphere of carbon dioxide to a temperature of 450° C. are used in match compositions patented by the Elektron Fabrik. Matches of this composition are less affected by moisture than those containing phosphorus sulphides. The addition of an ignition mass containing an inorganic non-combustible binding substance has been suggested for repeat ignitable matches.

B. SUBSTANCES WHICH SUPPLY OXYGEN

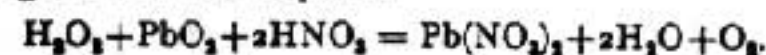
1. Minium or Red Lead (Pb_3O_4) is prepared by heating yellow lead oxide (massicot) in air to about 300°, when it absorbs oxygen and becomes converted into red lead. It has a sp. gr. of about 8.8. As the use of minium is solely dependent on its oxygen content, only the purest product should be used (with not more than 1 per cent. of impurity). This is tested by dissolving 1 g. in a mixture of 2.5 g. of nitric acid (sp. gr. 1.15), 3 to 4 g. of water and 0.5 g. of oxalic acid and filtering.

2. Lead Peroxide mixed with Lead Nitrate.—This "mixture" is prepared by treating minium with nitric acid of sp. gr. 1.384. A moderate amount of heat is evolved. Minium, whose composition may be written $2PbO \cdot PbO_2$, gives up the lead oxide (PbO) to the nitric acid to form lead nitrate, the peroxide remaining unchanged. Excess of nitric acid is to be avoided, as it not only acts on the binding substance in the match composition, but also renders the phosphorus inactive, by oxidising it to phosphoric acid. It also gives the mixture a thin consistency, whereas if the correct quantity of acid is used, the product is stiff and pasty. A badly made mixture contains too much lead nitrate, which causes the match-head to sweat, thereby producing a bad ignition and giving an unsightly appearance to the match-head. The product must also be free from lead chlorides and lead sulphate, which are avoided by using pure raw materials.

3. Lead Peroxide is prepared from red lead, by boiling it, in fine powder, with dilute nitric acid, washing and drying. It has a sp. gr. of 9.4. It readily parts with oxygen to other substances and hence is used in match compositions. The percentage of lead peroxide in a sample can be estimated by treating the peroxide with a measured

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volume of hydrogen peroxide previously acidified with nitric acid. The following reaction takes place:—



The undecomposed hydrogen peroxide is then determined by titration

with potassium permanganate solution.

4. **Lead Nitrate** is readily obtained in match factories by allowing the wash-waters, obtained in the preparation of lead peroxide, to crystallise.

5. **Manganese Dioxide**—

The value of the dioxide depends on the amount of available oxygen. Manganese dioxide is seldom used for phosphorus compositions, but is employed for safety and non-poisonous "strike anywhere" match pastes, and also on the striking surfaces.

6. **Potassium Chlorate**—

It is the most powerful oxidising agent used in the match industry, and the substitution of the very hygroscopic sodium chlorate for it is not to be recommended.

7. **Potassium Nitrate**—

It is essential that refined saltpetre only be used, as the crude salt contains chlorides which are deliquescent.

8. **Potassium Dichromate**—

It is used in the manufacture of safety-matches, and in very small quantities in the compositions of red phosphorus matches.

9. **Barium Nitrate, Strontium Nitrate**—These substances are used principally in pyrotechny (see p. 149).

10. **Calcium Orthophosphate (Ca_3PbO_4)** is a heavy yellowish-red powder prepared by heating calcium oxide and litharge to redness in air. It was first prepared by Kassner and was recommended as a substitute for lead peroxide and lead nitrate, in the manufacture of non-poisonous "strike anywhere" phosphorus matches. Schwiening's composition is used by match-makers, owing to the prohibition of the use of white phosphorus, and contains calcium orthophosphate, together with potassium chlorate, amorphous phosphorus, friction material, binding and colouring substances. The calcium phosphate appears to act as a negative catalyst on the explosive mixture of potassium chlorate and phosphorus, retarding the explosion, so that only inflammation occurs.

C. SUBSTANCES WHICH INCREASE FRICTION, INERT SUBSTANCES, OR FILLING MATERIALS

Among these substances are powdered glass, pumice stone, sand, chalk, plaster of Paris, pulverised asbestos, siliceous marl, Kieselguhr, powdered quartz, brown umber, Venetian red, zinc oxide and

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pulverised paper moulded with a binder, e.g. rubber solution or starch.

These serve, on the one hand, to increase the friction, and on the other to retard the explosion on igniting the match-head, so that the flame has time to act on the other materials, sulphur, paraffin, etc., which propagate the combustion. Brown umber is a variety of clay coloured by the oxides of iron and manganese. Venetian red is ferric oxide, Fe_2O_3 , and is obtained by the calcination of green vitriol. The use of chalk as a filling material is now rare. Zinc oxide is employed chiefly in the compositions of matches containing phosphorus sesquisulphide, red phosphorus and the like.

The above substances can all be obtained in the requisite degree of purity.

D. BINDING SUBSTANCES

1. Glue

1. THE COMPOSITION AND MANUFACTURE OF GLUE

Boiling water extracts from certain portions of vertebrate animals a material known as glue. These portions are the connective tissues and the intercellular substance of the sinews, ligaments, bones and dentine. A genuine glue contains mainly the complex nitrogenous organic substance gelatin. A number of other substances are often called glues: for example, starch glues, casein glue, marine glue, and various mineral and vegetable adhesives. The nature of glue is to some extent determined by the class of tissue from which it is made. The various tissues from which glue is obtained can be briefly classified

as follows: ossein in bones and skin, chondrigen of cartilage and isinglass from the bladders of fish. These three classes are included under the general heading of *Collagens*. *Chitin*, $\text{C}_{18}\text{H}_{39}\text{N}_3\text{O}_{11}$, is the main constituent of the shells of lobsters, beetles, crabs, etc. It is a white translucent substance, but has very poor properties as a binding material. *Keratin* is from horns, hair, nails, feathers, wool, etc., and remains after these materials have been treated with chemicals and solvents. These again are poor adhesives. *Sericin*, $\text{C}_{15}\text{H}_{25}\text{N}_3\text{O}_8$, is extracted from silk by boiling water under pressure. It resembles gelatin but is precipitated by lead acetate. *Elastin* is obtained from certain ligaments.

For commercial glues the tissues classified as the collagens supply the only practical raw material. The glues from this source may be classified as follows:—

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1. *Glutin* is the main constituent of commercial glue; it has the approximate composition:—

Carbon	50.0	per cent.
Hydrogen	6.6	"
Nitrogen	17.8	"
Sulphur	0.25	"
Oxygen (by diff.)	25.2	"
Ash	0.2	"

It swells up in water without dissolving. On heating it changes to a liquid and on cooling again gelatinises. It is soluble in acids and alkalis at laboratory temperature. On continued boiling with water, glutin loses its solidifying property (i.e. its property of gelatinising on cooling). It is not precipitated by acetic acid, potassium ferrocyanide or nitric acid, and in this way differs from the true albuminoids. Most varieties of tannic acid throw it out of solution.

2. *Chondrin* is somewhat similar to glutin, but is more horny in structure and its adhesive power is less. It is obtained by boiling cartilage with water; the resulting opalescent liquid gelatinises on cooling. It can be precipitated by dilute mineral acids but redissolves in excess. It is sometimes regarded as a mixture of glutin with mucin. Mucin is generally regarded as a mixture of complex organic substances which are generally removed during the liming process. They have practically no adhesive properties, and if present in glutin to any appreciable extent they give rise to foaming when the solution is warmed.

Commercial gelatin glues are divided into various classes, according to the raw products from which they are made, as follows:—

Skin Glue. For the manufacture of this glue, waste materials from the slaughter house are used. The inner skins contain a large amount of connective tissue which, on extraction with boiling water, yields glue. The first process consists of a treatment with lime or sodium sulphate in open, shallow pits for several days, with repeated agitation. The insoluble material is then washed and scraped to remove hairs and flesh. The cleaned material is next boiled with water in open vessels and the resulting solution (which contains the glue) is filtered and concentrated *in vacuo* at approximately 60° . The resulting dark viscous solution is decolorised by charcoal and sulphur dioxide and the hot filtered solution allowed to settle.

Leather scrap may also be utilised for glue manufacture by digestion with an aqueous solution containing 5 per cent. of sodium hydroxide on the weight of the dry leather scrap. The mixture is boiled until the glue-like substances are liberated, drained and filtered.

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The solution is then decolorised, if necessary, and concentrated. A clear glue can also be obtained by agitation with porous vegetable material of open texture, possessing approximately the same cellular structure as that of the material from which the glue is made. Kieselguhr may also be added and the filtered decolorised solution further concentrated.

Bone Glue. This type of adhesive is obtained from bones of various types. The fat is first removed by a restricted steaming in a

digester or by solvent naphtha or petroleum. To extract the glue the bones are heated under pressure with steam in special autoclaves. The calcium phosphate may be first removed by acids and the residue steam treated. The solution after clarification is concentrated *in vacuo*.

Fish Glue. Various types of fish offal are used and the treatment is somewhat similar. Glues of this type are generally deodorised to some extent by the use of sodium phosphate or otherwise.

The addition of potassium dichromate to the glue is stated to make the match composition gradually damp-proof owing to the oxidation of the glue.

A water-soluble albumin has also been proposed as an ingredient in the mixture for match-heads and striking surfaces. The binding agent containing a soluble albumin is rendered insoluble in water during drying of the composition.

II. PROPERTIES AND EXAMINATION OF GLUE

Glue is mainly used for its adhesive and binding properties. A good glue should be very hard and not readily brittle. When struck with a light hammer it should give a loud, sharp sound. It should be clear and transparent with a pale colour, with freedom from foreign particles. This latter property may give rise to mistakes, as the so-called benzine glues, although thin and pale-coloured, are, as a rule, inferior to true gelatins. When placed in cold water it should only swell and take up a large volume of water without dissolving; the water should have at most only a faint odour and should not show any appreciable cloudiness. On heating to 50° good skin glue should completely dissolve. Numerous methods are in use to test the quality of glue. Lipowitz estimates the bearing power of a gelatinised glue solution of definite concentration (generally 10 per cent.) at a definite temperature. The glue is placed in cylinders which are closed with a lid through which, in a guide tube, passes a stout wire, to the lower end of which is fixed a convex disc. On the other end is

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fixed a balance pan. The convex surface rests on the top of the jelly and weights are added until the lower disc penetrates. The greater the weight added, the greater the consistency.

Liquid Glue can be obtained by treating 100 parts of glue with 140 parts of water and 16 parts of nitric acid; it still retains the adhesive power of the glue used in its production, but does not gelatinise. This glue, and also liquid glue made with acetic acid, will not serve for the manufacture of match compositions.

Water Resistant Glue. The addition of formaldehyde polymerides or related compounds to animal glues produces a water resistant glue.

Examination. A weighed quantity of dry glue is allowed to remain for twenty-four hours in cold water, then allowed to dry and weighed again. The nearer the final weight approaches to the original, the better is the sample.

The desirable properties in a glue vary with the purpose for which it is to be used; the buyer often lays chief stress upon the binding power of the glue. As the determination of the binding power is difficult, Kissling devised the following simplified scheme for testing glue.

I. Kissling's Scheme for Testing Glue

1. **Determination of Moisture.** A sample is removed from the slab of glue with the aid of a coarse wood rasp, 2 to 3 g., quickly weighed out on to a large watch-glass, and dried to constant weight in an air-oven at 110° to 115°. It is absolutely necessary to carry out the drying with finely powdered glue, for the moisture cannot be completely expelled at the above temperature from larger particles, and it is advisable to resort to a higher temperature. The moisture content of a good glue is generally between 10 to 20 per cent. A lower result indicates that the glue has been overheated in drying and the adhesive properties may be affected. Powdered glue loses very perceptibly in weight, if allowed to stand in the laboratory at the ordinary temperature for some time.

2. **Determination of Ash.** For the determination of the ash it is convenient to use the same sample of glue as was taken for the moisture determination. It is incinerated in a covered platinum or silica crucible, the full heat of a Bunsen burner being at once applied. The traces of mineral matter which are lost in this shortened method may be neglected without danger, since only great differences in the quantity of ash need be taken into account. The last particles of carbon, which are somewhat difficult to remove, are best burnt by repeatedly allowing to cool, moistening, and igniting the contents of the crucible.

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3. **Qualitative Examination of the Ash.** The nature of the ash generally gives reliable indications as to whether the glue was derived from bone or from hide. The ash of bone glue melts at the temperature of the Bunsen burner, its aqueous solution generally reacts neutral, and its solution in nitric acid gives the reactions for phosphoric and hydrochloric acids. If the ash has been very strongly ignited, deposits of alkali chlorides are found on the inside of the crucible cover and sometimes on the edge of the crucible. The ash of skin or hide glue contains a large proportion of lime and remains therefore unmelted. It reacts strongly alkaline and is generally free from phosphates and chlorides. An unadulterated glue should have an ash content of approximately 2.5 per cent. or less.

4. **Determination of Alkalinity.** To 2 g. of glue, dissolved in 18 g. of water, is added 40 g. of 99 per cent. alcohol; after brisk agitation, the mixture is filtered and titrated with *N*/10 hydrochloric acid, phenolphthalein being employed as the indicator.

5. **Free Mineral Acid** is determined by titrating a 10 per cent. solution of the glue in water with aqueous sodium hydroxide solution, successive portions of the liquid being spotted on to neutral litmus paper. The quantity of alkali to be added each time before the spotting must correspond to 0.005 g. H_2SO_4 . During the titration, the glue solutions are warmed to about 30°. Phenolphthalein may be used as indicator.

6. **Determination of the free and combined volatile Acids.** Thirty g. of the glue is covered with 80 g. of water in a round-bottomed flask and placed aside for a few hours to allow the glue to swell. An arrangement is then fitted up which permits of the removal of the volatile acids by steam distillation, the flask being conveniently placed in a vessel containing boiling water, in order to avoid the condensation of any considerable quantity of steam. As soon as the distillate no longer has an acid reaction, the distillation is stopped, and the quantity of acid is determined by titration. To liberate the combined volatile acids, the contents of the flask are next acidified with concentrated sulphuric acid, and distilled again in a similar manner. In some instances the distillate contains considerable quantities of sulphurous acid, so that it is advisable to distil into a known quantity of standard alkali. The sulphurous acid can be converted into sulphuric acid by the addition of bromine, and then determined gravimetrically. The acid content of a good glue is generally less than 0.2 per cent.

7. **Determination of the Drying Properties.** The solution of glue, freed from volatile acids, is diluted with water to a weight of 150 g. and again heated to the temperature of boiling water with an upright tube to prevent loss by evaporation. Ten c.c. is then withdrawn by a pipette on to the middle of a watch-glass of about 10 cm. diameter, in

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such a way that no glue is present on the glass outside the circular disc of jelly, the centre of which must coincide with that of the glass. The watch-glass is placed in a horizontal position before the addition of the glue; it should be allowed to remain in a place as free as possible from dust and draughts, and where the temperature is not liable to fluctuate greatly. The alterations of the glue are then observed for a few days. According to the drying properties of the glue, the jelly dries more or less quickly from the edge to the centre, and from the size of the patch which still remains soft after a certain time, a fairly reliable conclusion can be drawn as to the drying properties of the sample. As the process

of drying is greatly influenced by the degree of moisture and temperature of the air, and as it is very difficult to keep these constant, it is advisable always to carry out comparative determinations. It is, therefore, advantageous to compare the glue under examination with two samples which have been previously tested, one of good, and the other of inferior drying properties, the three being treated identically, as above.

8. *Determination of Foreign Matter.* Kissling recommends only an approximate quantitative determination of the total quantity of those substances which are deposited when the glue solution is sufficiently diluted. The separation of these substances by filtration is troublesome and slow, even after partial separation by decantation, so Kissling makes approximate determinations of the volume of the solid deposit, since the estimation is only comparative. The glue solution referred to in (7)—that is to say, 150 c.c. less 10 c.c.—is diluted with hot water, allowed to cool, introduced into a cylinder of 1000 c.c. capacity, graduated in c.c., filled up to the mark, mixed and allowed to stand. The volume of the solid deposit, after twenty-four hours, forms a measure of the quantity of insoluble "foreign matter" in the glue. This is generally very small, but in some cases considerable. Such substances decrease the binding quality of the glue when they consist to a great extent of organic matter.

9. *The Odour.* This feature is of especial importance, as it gives indications concerning the durability of glue, and its tendency to decompose. The smell of glue varies greatly according to the quality. Usually, hide glues are in this respect superior to bone glue. With some kinds of glue, the smell of the cold slabs is very slight, whereas the hot jellies have a very unpleasant smell. In such cases the glued surface, after drying, has a much more unpleasant smell than the cold slab. In his published results, Kissling therefore gives indications of the smell, both of the dry glue and of the hot jelly. Obviously, it is only possible to judge the odour accurately after carrying out a long series of investigations of glues.

In general a satisfactory agreement has been found between the

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results of practical experience and those of Kissling's tests. The amount of acidity determines the suitability of a glue for some purposes. The quantitative estimations of water, ash and fat (see p. 111) are generally of minor importance. Hide glues show a superiority over bone glues, but it must be emphasised that the manufacture of bone glue has undergone such improvements that its relative value in comparison with hide glue has greatly increased. The best bone glues now compare approximately with medium skin glues.

In a subsequent publication, Kissling emphasises the fact that all forms of apparatus devised for the purpose of directly measuring the binding power, the first requirement in the testing of glues, fail to give even approximately concordant results under identical conditions of experiment. This is, at all events, his experience with apparatus devised by himself for this purpose (*loc. cit.*), and for this reason he prefers the determination of the drying properties of glue. In a later paper he strongly advocates, and describes an apparatus for, ascertaining the melting point of the glue jellies.

The main conclusions from a paper by E. G. Clayton, on the technical examination of glue, based on investigations of a number of samples of British and foreign origin, are as follow:—Colour is of limited value as an indication of quality, and too much importance is often attached to it. Some dark-tinted glues may be better in quality than comparatively pale samples. Air bubbles should be few, or better, absent. The odour of samples should be inoffensive. Good glue should not deteriorate quickly on exposure. Physical tests usually lead to more definite conclusions than analyses, but some of the chemical data are very useful. Perhaps the best *single* chemical test is Stelling's—the determination of non-gelatinising matters by precipitating with alcohol, filtering, evaporating a fractional part of the filtrate, and weighing the dried residue. A high result appears to be a *prima facie* indication that the glue, at all events, is below the best standard of quality. Hygrometric, immersion, jelly-drying, viscosity, and other tests are described in the paper. The viscosity test and

Kissling's jelly-consistency test are favourably reviewed, and the hygrometric test (rate of absorption of moisture from air saturated with aqueous vapour) is stated to give useful indications. Finally, it is remarked that whilst it would be rash to form a judgment on glue from a single test, the evidence afforded by a number of tests may be decisive.

The hydrogen ion concentration of a glue may often be an important determination as giving an opinion of the value of such product,

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according to Bogue. If the pH value is 4.7 the viscosity will be low and the product nearly insoluble. On either side of this point the properties change considerably, attaining their maximum on the acid side at pH 3.5 and on the alkaline side at pH 9.0. The measurements may be made by electrometric or colorimetric methods.

2. Methods for the Determination of Fat in Glue

W. Fahrion recommends the following process:—Ten g. of broken glue is warmed on a gently boiling water-bath with 40 c.c. of 8 per cent. alcoholic sodium hydroxide in a porcelain dish, with constant stirring, until the alcohol is completely driven off. If complete solution does not occur, the residue is taken up with alcohol and again evaporated to dryness. The transformation product of the glutin, as also the sodium salts of the fatty and hydroxy-fatty acids dissolve readily; any residue which is found, consists of inorganic matter, and dissolves on subsequent acidification with hydrochloric acid. The acidified solution is heated for about half an hour almost to boiling, then washed into a separating funnel, and after cooling, well shaken with ether and allowed to stand for a considerable time, best over night. The acid aqueous liquid is drawn off, and the ethereal solution which contains the fatty acids and the liquid hydroxy-fatty acids is poured off at the top. The solid hydroxy-acids which remain behind in the funnel are dissolved in warm alcohol, the ethereal and alcoholic solutions combined and evaporated, the residue weighed, ignited, and again weighed and the difference taken as the fat. The results obtained in this way agree satisfactorily among themselves, but are always too low, for two reasons. Firstly, any glycerin present in the glue fat is not determined with the fat, and secondly, the hydroxy-acids are not quite insoluble in acidified water. The error which results in this way is, however, very small.

For instance, the quantity found for a brown joiner's glue by Kissling's method was 0.21 per cent., by Fahrion's method, 0.51 per cent., and in an almost white skin glue, by Kissling's method, 0.13, and by Fahrion's method, 0.40 per cent. of fat.

According to Kissling's method (shaking out the glue solution, with petroleum ether after acidification with hydrochloric acid), only that part of the fat which is soluble in petroleum ether, is determined. The fat contained in glue is, however, partly oxidised, and oxidised

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fats are in some cases insoluble in petroleum ether. The raw materials for the manufacture of glue, namely, skin and bones, already contain oxidised fat. Further, the glue decoction is repeatedly heated in presence of air, and finally the drying of the glue brings it into such intimate contact with the air that the oxidation of the fat probably proceeds further. Indeed, Fahrion found in a skin glue only 0.08 per cent. of fatty acids as compared with 0.31 per cent. of oxidised fatty acids.

3. Differentiation of Animal and Vegetable Glue

F. Evers has published an investigation on the differentiation of animal and vegetable glue. The distinction between animal glue and dextrin glue, or between gum and mixtures of gum or dextrin with animal glue, is based upon the well-known reaction towards Fehling's solution, which is reduced in presence of dextrin on boiling. So-called plant glue (albumin glue, gum), which is prepared from wheat gluten and is used for gumming and cloth dressing, is very similar to animal glue in its physical and chemical properties, particularly to inferior bone glue. Its aqueous solution gives, like animal glue, a voluminous

gelatinous or cheesy coagulum with tannin solution; with a little aluminium sulphate solution it gives no precipitate, or at the most only a slight separation, but with larger quantities of aluminium sulphate it yields a greater amount of a flocculent or cheesy precipitate, whilst with lead acetate it undergoes no change. In general, vegetable glue swells and dissolves with more difficulty in water than animal glue, and the solution gelatinises less readily on cooling. A trustworthy method for distinguishing between the two cannot, however, be based upon this property. Both animal and vegetable glue give flocculent precipitates with concentrated sodium sulphate, which, however, redissolve on warming. If the solution be boiled for some time and treated with lead acetate, animal glue gives a white or pale grey precipitate, while vegetable glue, containing as it does, larger quantities of sulphur, generally gives a black precipitate, less frequently a grey one. An aqueous solution of vegetable glue gives on warming with Millon's reagent a violet-red coloration, like all albuminoid substances; in many cases, however, inferior animal glue behaves in the same way.

A simple and trustworthy method for distinguishing between animal and vegetable glue is the following:—The sample of glue (about 1 g.) is dissolved in water (10 c.c.) by warming, a drop of sodium hydroxide solution being added if necessary. A few grams of common salt or magnesium sulphate are then added, and the whole shaken. The

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solution of animal glue remains clear, whilst vegetable glue separates almost completely as a voluminous or gelatinous precipitate. Mixtures of animal and vegetable glue can be readily recognised in this way.

4. Physical Tests

The physical examination of glue, especially viscosity, rate of drying, gelatinisation point, joint strength, elasticity, etc., are important and are often determining factors in judging the value of a glue.

(a) *Viscosity*.—According to the investigations of Fels, the consistency of glue is closely related to the quality or binding power. Neither the quantity of water taken up, nor the examination of the mode of fracture gives trustworthy indications of the practical value of a glue, but the viscosity of the solution is a better index of quality. The reason of this is evident; glues which have been prepared under the influence of lime or acids give rise, under certain conditions, to a less consistent jelly than a properly manufactured product, namely, when the lime or acid has not been sufficiently carefully removed from the glue. The decomposition products which result in presence of lime or acids, especially on boiling or steaming the glue-producing substance, as also those which result when too high a steam pressure has been used, diminish the consistency of the jelly, as does also a badly regulated concentration of the glue solution, or even an incipient organic decomposition of this solution.

All these influences affect the finished product, and if the degree of consistency of the jelly obtained from a glue be examined, a true measure for adjudging the quality is obtained. The method is very simply carried out as follows:—

1. *Determination of Moisture*. The sample is broken up, 1 to 2 g. of powdered glue obtained from the fragments, with the help of a file, rasp, or knife, and this quantity is dried for two hours at 100°.

2. *Preparation of the Test Jelly*. About 100 g. of the glue under examination (viz. the broken pieces from which the fine powder was filed) is placed in a beaker of 500 c.c. capacity, and about 400 c.c. of cold water added; after twenty-four hours the swollen glue is dissolved by heating on a water-bath. The dilution is carried out in such a way that a 15 per cent. jelly results, calculated on the anhydrous glue.

Clark and Du Bois describe a physical test for glues. It consists in determining the weakest solution of the glue which gives a solid jelly at 10°. If a 6 per cent. solution of the substance is liquid and a 7 per cent. solution is solid, the jelly is said to have a comparative jelly value of 7 per cent. The comparative strengths of glue jellies

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can be found by determining the ease with which swollen particles of

glue melt and slide when placed on a sloped brass plate. The lower end of the plate is dipped into water and kept at 40°. The better glues retain their grip on the plate for the longer period.

3. *Determination of the Viscosity*. Engler's viscosimeter is especially good for this purpose. First, the viscosity of water at 30° is determined, and used as a unit for the subsequent glue tests. The same determination is then carried out with the 15 per cent. solution of glue, also at 30°. The time of flow of the latter divided by that of water gives a number which expresses the consistency of the glue.

Some results obtained by this method of examination are given in the following table. Sample No. 2 was quite slimy after a few hours and sank together to a lump, whereas No. 5 preserved its original form and gave up no particles of jelly, even when scraped with the finger. Further, it was found that Nos. 3 and 5 became a solid jelly after twelve hours, whereas No. 2 was still a thin jelly, and underwent no alteration even after a further period of twenty-four hours:—

Description of sample.	Substance used, in grams.	Moisture content per cent.	Corresponding quantity of anhydrous substance.	Dissolved in c.c.	Time of outflow of 500 c.c. in seconds.	Viscosity.
1. Light yellow, transparent thick slabs.	95.0	16.3	79.6	530	149	1.65
2. Brown glues, transparent	95.0	14.0	81.7	544	125	1.38
3. Wine yellow, transparent slabs.	88.7	15.4	75.1	500	171	1.90
4. Light yellow slabs, breaking into small pieces.	100.0	18.2	81.8	545	150	1.86
5. Semi-opaque glue.	100.0	15.2	84.8	565	199	2.21

In the MacMichael viscosimeter a plunger of standard size is used, suspended by a torsion wire above the instrument. The glue is placed in a cup which is rotated at a constant speed on a motor-driven platform. The viscosity determines the twist on the wire which is measured by a disc attached to the spindle.

The viscosity of gelatin and glue is affected by the acidity of the material, by the age of the solution, and by other factors. A method of testing glues suggested by Lenk consists in measuring the time of gelatinisation in minutes at pH 7.0–7.5. He proposes the

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formula $y = -0.55x + 1.8$, where $x = \log.$ of gelatinisation figure in minutes and $y = \text{viscosity}$.

Goebel determines the viscosity of hide and leather glues in 17 per cent. solution at 40°, and of bone glue at 30°. He uses either an Engler or Vogel-Ossay instrument and determines the concentration by means of a Suhr glue hydrometer calibrated in percentages.

(b) *Melting Point of the Glue Jelly*.—Kissling considers that such chemical methods as precipitation with tannin, or estimations of the percentage of nitrogen, are unsuitable for adjudging the value of a glue.

A bath of copper or other metal partially filled with water at 50° serves as the source of heat. The bath should be filled to a mark placed at two-thirds of its height, and the temperature is kept constant during the experiment. The bath is fitted with a removable cover consisting of a vessel, the bottom of which is covered with a sheet of asbestos upon which rests a ring-shaped receiver. In this a thermometer and the small cylinders containing the glues are placed. The upper vessel is covered with a glass plate. It is advisable to cover the outside of the vessel with asbestos. The method of working is as follows:—Fifteen g. of the glue samples to be tested and 30 g. of distilled water are introduced into small flasks, each fitted with a straight tube about 1 metre long. The flasks are allowed to stand over night and then heated in boiling water until the glue has dissolved completely, solution being accelerated by shaking the flasks with a circular motion. The flasks containing the lukewarm glue solutions are then fitted into the glass cylinders, which are made exactly to a specified

size and are provided with ring-shaped marks; the cylinders are closed with corks and placed in a holder, the base of which consists of a brass sieve, over which two intermediate discs are fixed, each containing seven holes. The cylinder containing the thermometer is placed in the middle, and contains a concentrated solution (1:1) of the best hide glue. The receiver thus filled is allowed to stand for an hour in water, the temperature of which is kept at 15°. After the thermometer vessel and test cylinders have been thus brought to the same temperature, they are quickly brought into the thermostat, which has been

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fitted up as above, and the melting point of the glue jelly determined. The melting point is the temperature at which the horizontal surface of the jelly begins to become uneven. The higher the melting point, the higher is the content of gelatinising substance. In addition, this simple method gives direct indications as to the degree of firmness of the glue jelly, which is of importance in certain cases, as, for instance, in glueing casks.

As regards the testing of plates of glue, the question whether a glue is good or bad, useful or useless, cannot be answered in a general way unless it is so inferior in quality that it can be discarded at once as worthless. In the great majority of instances the purpose for which it is to be used must be known; hence a glue can only be designated as unsuitable for a specific purpose.

So far as the binding properties are concerned, numerous experiments have shown that even inferior bone glues are satisfactory, and hide glue of high quality scarcely shows any superiority in this respect. If, therefore, only the binding properties have to be taken into consideration, there is no object in using the more expensive hide glues. This does not hold good for the degree of firmness. Experiment has shown that hide glues are in general superior to bone glues in this respect, although some samples of the latter yield moderately firm jellies. As is well known, the method of manufacture plays an important part in reference to this property; the larger the quantity of glutin that is converted to glucose during the manufacture, the less firmness does the jelly possess, and in this respect the manufacture of bone glue has undergone great improvements.

Considerable weight is attached by some writers to the "Foam-test." Foam is due to over-boiling, which causes peptonisation. A good glue, it is stated, should yield a minimum foam, when the solution is shaken, coupled with a maximum jelly consistency.

(c) *The Binding Power.—Setterberg's Method.* This author soaks strips of unglued paper in a glue solution of known concentration, removes the excess of glue by pressing between blotting paper, and when dry, estimates the binding power of the glue by subjecting the strips to tearing tests in a paper-testing machine.

2. The adhesive power of glue can be determined by the method of Rudeloff. A standard aqueous solution of the glue is applied to two wooden surfaces of definite areas. The surfaces are previously cleaned and dried at 40°. Two wooden glued surfaces are placed in contact, and the films allowed to make contact at a pressure greater

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than 0.84 kgm. per sq. cm. The force required to separate the glued surfaces after a definite time is then measured.

3. *Weidenbusch's test for Binding Power.* This test gives reliable results. Exactly equal prismatic rods of plaster of paris, 9.2 cm. long, with the side of the transverse section 4 mm., and having a weight of 1.7 g., are dipped in a glue solution for five minutes, then taken out, and allowed to dry. They are then placed on an iron ring, which is fastened in a horizontal position, so as to form the diameter; a dish is hung to the centre of the rod, into which weights are placed until the rod breaks. The better the glue, the greater the weight required to break the rod. By experiment it has been found that the relative adhesive power of skin glue to that of bone glue, is as 1.5:1; and, further, that glue made from calves' head is better than any other class of glue. The following table bears out these facts:—

Class of glue.	Breaking strain.	Appearance of fracture.
	Grams.	
Glue from crushed bones, Saybusch	291.6	Even, four-sided.
Russian glue from Bohemia	304.2	Even, fine-grained.
Saybusch glue, Lyon class	351.2	Slightly uneven.
Russian glue from A. Michl, Rehberg	434.2	Uneven, with sharp projecting edges.
Cologne glue from A. Michl, Rehberg	434.2	Do.
Glue from calves' heads, from Saybusch, Lyon class	483.7	Do.
Plaster of paris rod before dipping in glue	103.2	Fairly even, fine grained.

Evaluation of a Glue from Viscosity Tests. The chemical analysis of a glue generally does not greatly help in its evaluation. The examination of moisture, ash and water adsorption give some information regarding the nature of the glue, but other tests are necessary, particularly those of a physical nature. The jelly consistency at low temperature or the viscosity at high temperature give useful comparative figures. Bogue recommends the measure of the viscosity of an 18 per cent. solution at 35° by means of the MacMichael viscosimeter as an indirect test for the differentiation of glues and gelatins. It is recommended as a basis for the primary evaluation of these products. Tests of jelly consistency and viscosity at 60° are recommended for secondary evaluation.

For the rapid determination of the quantity of glue or gelatin in dilute liquors for the control of manufacturing processes physical methods are essential. Measurements of refractive index have been found very suitable.

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Frei used the Pulfrich refractometer with a single cell. Walpole and Hart used the Zeiss immersion refractometer. According to Kane and Watson, in order to obtain the full accuracy of which the Pulfrich refractometer is capable, it is necessary to know the compensation very closely. They overcame this difficulty by working with a double cell, one compartment being filled with distilled water and the other with the solution under examination. If this be done, provided sufficient time is allowed for the two liquids to reach the same temperature, it is only necessary to read the difference in refractive index on the micrometer and the temperature need not be measured at all. The method has the additional advantage that, owing to the position of the edge of the line being to a slight extent a matter of personal judgment, more accurate settings are possible when made on two lines in quick succession than when a considerable interval elapses between the readings.

The following results illustrate the accuracy of the method as worked out by Kane and Watson. Kahlbaum's "Gold Label" gelatin was employed with a water content of 17.5 per cent., and ash 1.8 per cent. Solutions were made at 60°, filtered, and the gelatin determined by evaporation to dryness and heating at 105° for 15 hours. More dilute solutions were prepared from the original by adding weighed quantities of water. The difference between the refractive index of the solution and that of distilled water was then read on the micrometer of the refractometer. Consecutive readings were found to differ by not more than 6 secs. The table below gives the concentration of the

Refractive Index of Gelatin Solutions at 21° and 29°.

G. gelatin per 100 g. water.	G. gelatin per 100 c.c.	Difference in micrometer readings.	$\delta n_D \times 10^6$	$\delta n_D \times 10^6/\text{g. weight.}$	$\delta n_D \times 10^6/\text{g. volume.}$
21°					
0.122	0.122	2.80	22	180.0	180.0
0.202	0.201	4.65	37	183.0	184.0
0.320	0.318	7.30	58	181.0	182.0
0.526	0.524	12.15	96	182.0	183.0
0.710	0.706	18.25	130	183.0	184.0
0.879	0.872	19.95	159	181.0	182.0
1.330	1.316	30.10	240	180.0	182.0
1.784	1.764	40.40	323	181.0	184.0
29°					
0.780	0.772	18.15	143	183.0	185.0
1.130	1.116	26.10	207	183.0	185.5
1.592	1.566	36.60	291	183.0	186.0
2.408	2.356	54.95	439	182.6	186.3
3.216	3.137	72.85	584	181.7	186.2

solutions, the difference in micrometer readings, the change in refractive index, which is not quite a linear function of the angular difference, and the change in refractive index per gram of gelatin for different concentrations. All measurements were made at room temperature, the first series during cold weather in the neighbourhood of 21° and the second series in hot weather at approximately 29°.

The concentration of gelatin has been given both in grams per 100 g. of water and grams per 100 c.c., the latter being calculated by Kane and Watson by means of Davis and Oakes' formula, $D_x = D_0 + 0.0029x$, for the density of a solution containing x per cent. of gelatin. It will be seen that the relation between change in refractive index and concentration is very nearly linear whichever method of expressing the latter quantity is adopted, the variation being slightly less for volume concentration. The actual values for change in refractive index per gram of gelatin agree closely with those of Walpole (182.4 at 17.5° for solutions up to 4 per cent.) and Hart (mean for different specimens of glue at 20°, 183).

5. Commercial Varieties of Glue

Joiners' Glue is either skin glue or bone glue, or a mixture of the two. *Cologne Glue* is the best and purest skin glue, and is very much in request on account of its high adhesive power. *Gilders' size* is Cologne glue in thin leaves bleached by chlorine. *Patent Glue* is a pure, dark-brown bone glue in thick tablets, without net-markings; it swells greatly in water, and serves for mouldings, buttons, and the like. *Fining Glue* is manufactured from bones in the form of thick, pale-tinted plates, and is used instead of isinglass for the fining of wine and beer. *Mouth Glue* is a better quality of bone glue, scented with lemon essence and sweetened with sugar. *Russian Glue* is a dingy white or brownish-white variety of Cologne glue, rendered opaque by the addition of white lead, zinc white, permanent white, or chalk. An improvement in adhesiveness is not aimed at by the additions.

Glazing and parchment size are valuable kinds of pure skin glue, resembling gelatin; parchment size is put on the market in jelly form, packed in small jars, usually with an addition of alum. *Flemish Glue* consists of thin, yellow leaves, shrunken in both directions, and is used for the production of glue colours and as a glazing material. *Paris*

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Glue and Hatters' Glue are poor, dark brown, opaque, almost always offensively smelling, soft varieties, used in hat-making because of their considerable hygroscopicity.

Liquid Glue. Thirty-eight parts of glue are dissolved in 100 parts of acetic acid; the resulting product remains in the fluid state. A preparation made with nitric acid is known as *Steam Glue*, also as *Russian light and dark Steam Glue*. *Glycerin Glue* is obtained by dissolving glue in warm glycerin; small additions of glycerin to steeped glue impart elasticity to the jelly, making it caoutchouc-like and suitable for hectograph compositions. *Chrome Glue* is either a mixture of glue with potassium or ammonium dichromate, or of glue with chrome alum. After drying, the former mixtures are insoluble in water. They are used for cementing glass, porcelain, and iron, for finishing and waterproofing materials, and for photographic purposes.

2. Gums

Three sorts of gums are used in the manufacture of matches—gum arabic, gum senegal and gum tragacanth.

(a) *Gum Arabic* forms irregular, brilliant, transparent, brittle pieces of a white to yellow or brown colour and varying from the size of a lentil to that of a walnut. The pieces are mostly filled with internal cracks, and are also cracked on the surface, which renders them easy to break and to powder. They do not become damp in the air, show a brilliant conchoidal fracture, and give with cold water an almost clear, viscous, slimy, slightly opalescent solution, which can to some extent be drawn out into threads, but which is neither

tough nor gelatinous. The solution reacts faintly acid and is very adhesive. Gum arabic breaks up and dissolves easily in the mouth, and has an insipid and slimy taste. The solutions are thick flowing and have a good adhesiveness.

On account of its high price, it is frequently adulterated, mostly with insoluble cherry-gum, dextrin, etc., and is sometimes bleached with sulphurous acid to make it appear of better quality for certain purposes. This renders it unsuitable for the manufacture of matches. Since the conditions of export from the Sudan have become unfavourable, gum arabic is adulterated with gum senegal; indeed, according to Liebermann, the latter is often sold as gum arabic. The solution, which is generally slightly acid, is heterogeneous.

(b) *Gum Senegal* forms round fragments which are larger and more transparent than gum arabic, and have fewer cracks penetrating to their interior. The pieces frequently contain large air bubbles,

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formed like tears, their surface is rough and not brilliant, they vary in colour from almost white to reddish-yellow, and their fracture is coarsely conchoidal and very brilliant. It is more difficult to dissolve than gum arabic, the solution is more gelatinous and less adhesive. It mixes well with organic acids and with alkalis.

According to Liebermann, gum senegal forms either colourless pale yellow, or superficially white pieces, resembling etched glass in appearance, which, however, are bright and transparent internally. The pieces are generally long, straight, coiled, or cylindrical with concentric rings. Roundish fragments of various sizes are, however, also met with, which have the appearance as if a large drop had become incrustated with smaller pieces after solidifying.

If the gum under examination has not been artificially powdered (by pounding), it is sufficient to observe these external properties to distinguish gum arabic from gum senegal. Other gums can also be detected, in this case, according to Liebermann, by the deviation of their appearance from the above.

Gum senegal is said to be distinguished from gum arabic, apart from the above method, by its property of gradually becoming moist on exposure to the air, as also by the fact that it gives only a slight turbidity with mercurous nitrate, and is very markedly thickened by borax. According to Liebermann and Kramsky, however, the assertion that gum senegal is more hygroscopic than gum arabic is incorrect. The percentage of water in each kind of gum was determined at 105°, and the dried substance allowed to stand for twenty-four hours in moist air and again weighed. Gum arabic proved to be slightly the more hygroscopic of the two, as shown by the following data:—

	Gum senegal.	Gum arabic.
Water	13.39 g.	14.56 g.
Water absorbed in twenty-four hours by the dried samples	6.15 g.	6.34 g.

Gum senegal coagulates with a number of chemical reagents, for which reason match-heads prepared with this gum are often not very cohesive.

(c) *Gum Tragacanth* comes into commerce in many different varieties. It is tasteless and inodorous, transparent, horny and tough, so that it is difficult to powder. Only a small part actually dissolves in water; for the most part, it swells up, forming a mucilage, which is not sticky, but nevertheless is highly adhesive, and can be mixed with water if in sufficient quantity. It is therefore added to the igniting composition for matches (especially safety-matches) in small quantities, firstly, in order to keep the heavier particles in

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suspension, and secondly, to impart greater hardness to the glue or gum-mass after drying, and thus to protect it from climatic influences. In the preparation of mucilage from gum tragacanth a short boiling gives a more viscous solution. Prolonged boiling decreases the viscosity.

It is advisable to dry the tragacanth very thoroughly, as this renders it more brittle, and facilitates the grinding. It should be coarsely

ground, because it then dissolves more readily, or rather, swells more uniformly and quickly.

Powdered tragacanth gives a turbid mucilage with 30 parts of water, and this is coloured yellow by sodium hydroxide, when the mixture is heated for a short time on a water bath. At ordinary temperatures, both powdered tragacanth and the mucilage prepared from it remain completely colourless for hours, on addition of sodium hydroxide. (Reuter.) The better the quality of the gum the more readily is it precipitated by solutions of sodium hydroxide or by borax.

A cheap substitute for tragacanth, discovered by Boschau, is a mixture of 20 parts of starch, 6 parts of glue, and 2 parts of glycerin, boiled in water, which is stated to be quite as efficient as tragacanth in its action. Semi-soluble gums and various mucilages such as that from Carraghin moss or Iceland moss have practically no application in the match industry, as they are difficult to prepare without suspension and they easily ferment.

There is no direct chemical method of determining the values of gums. The following, however, are useful tests and give some information regarding the gums: (a) ash content, (b) acidity, (c) moisture content, (d) keeping property of the gum. A good procedure to follow in testing is as outlined by Garner. The moisture is determined by heating 1 g. at 110° for four hours. Absence of moisture may indicate too friable a condition, so that the gum may powder too readily. The dried sample is then ignited, when the ash content should be less than 3 per cent. A larger value would indicate mineral addition. The ash consists mainly of the carbonates of calcium and magnesium. According to Garner the most important test in the evaluation of gum is the viscosity test and he recommends the following method in carrying it out.

Four g. of a typical sample of tragacanth is added to 50 c.c. water and allowed to steep for two days. The volume is then made up to 500 c.c. and the liquid passed through fine muslin. The resulting sieved mucilage is allowed to stand for an hour to become homogeneous. The viscosity is then determined in the usual way with a Redwood's viscometer. The calculations are as follows:—

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A is standard sample at P shillings per cwt. B is outside sample at Q shillings per cwt. 50 c.c. of an x per cent. solution of A takes x secs. 50 c.c. of a y per cent. solution of B takes y secs. Then 100 parts by weight of A give the same viscosity as $\frac{100x}{y}$ parts of B, and hence the equivalent weight of B to give the same viscosity as 100 parts of A should cost $\frac{Qx}{y}$ shillings. This relation only holds when the difference between x and y is only a few seconds. For greater differences the stronger solution should be diluted before determination of the viscosity.

3. Dextrin

Dextrin is obtained by the treatment of starch with dilute acids, or by prolonged heating of the mixture with water to from 200° to 250°. It forms a white, yellow, or brown powder, according to the method of preparation and the temperature employed, and should be completely soluble in water. The solution is optically active; its specific rotation $[\alpha]$ is approximately +200. Several varieties of dextrin are known. Variation in the treatment of the starch breaks down the complex polysaccharide to various stages, so that the term dextrin does not represent a single substance. The more drastic breakdown gives products which do not give a reddish-brown colour with iodine. The presence of any maltose, which is recognisable by its sweet taste, renders the dextrin useless for the manufacture of matches, since maltose makes the match-heads hygroscopic and ultimately incapable of ignition. White dextrin is almost useless for this purpose, the most suitable apparently being of a light brown colour. Dextrin should not be hygroscopic; it should be inodorous, insipid in taste, and should form a mobile powder which is easily soluble in water. Dextrin is insoluble in alcohol.

The aqueous solution should be colourless, completely clear, and neither acid nor alkaline. It should give no blue or violet colour with iodine solution, no turbidity with lime water, and no precipitate with

tannic acid and baryta water (soluble starch), or with lead acetate. When heated on platinum foil, it should burn without any residue. A blue or violet coloration with iodine indicates unaltered starch or soluble starch. The presence of lime is detected by the addition of ammonium oxalate, oxalic acid by lime water, gum arabic or mucilage by lead acetate. It does not form an osazone with phenylhydrazine.

Hanofsky recommends the following procedure for testing commercial dextrin:—

1. *Determination of the Constituents Soluble in Cold Water.* Twenty-five g. of the substance shaken with cold water in a flask of 500 c.c. capacity, filled to the mark allowed to settle, filtered through a folded filter and the solution used for the determination of maltose,

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dextrin, and acidity. The maltose is best determined gravimetrically by Fehling's solution, the solution being boiled for five minutes. The solution is diluted to a quarter of its original strength (10 c.c. Fehling's solution and 40 c.c. water). A preliminary determination is made, to determine how much of the solution is necessary to reduce 10 c.c. of Fehling's solution, and in the second determination, 1 to 2 c.c. less than this quantity are taken and diluted until the whole volume is 57 to 58 c.c.; 113 parts of copper correspond to 100 parts of anhydrous maltose; hence, when the solution is diluted to one fourth, 113 parts of copper correspond to 91.3 parts maltose, or 1 part of copper corresponds to 0.80 parts of maltose, from which the content of maltose M per 100 g. of the original substance is calculated. For the determination of the dextrin, 50 c.c. of the solution (or 100 c.c. if the quantity of insoluble matter is large) are diluted to 200 c.c. and boiled gently under a reflux condenser with 15 c.c. of hydrochloric acid of sp. gr. 1.125 for two hours. The liquid is then neutralised in a flask of 300 or 500 c.c. capacity, diluted to the mark, and the dextrose determined with Fehling's solution. If the quantity of dextrose found in 100 g. of substance is D, the quantity of dextrin present in the original substance is 0.9 (D-1.05 M), since 20 parts of dextrose correspond to 19 parts of maltose. The acidity is determined by titrating 50 c.c. of the solution with N/10 potassium hydroxide, using phenolphthalein as indicator. A certain error is introduced, if the volume of the residue in the flask is neglected, but in most cases it is unnecessary to take this into account. If, however, the quantity of insoluble matter is very great, a correction should be applied. If the sp. gr. of the residual starch be assumed to be 1.6, the volume of liquid to be deducted from

500 c.c. is, $V = \frac{p}{1.6}$, where p is the quantity of starch in 25 g. of substance. If the quantity of starch is 40 per cent., this volume is only 6.2 c.c.

2. *Determination of the Insoluble Matter.* This consists almost exclusively of starch. Two and a half to three g. of substance is boiled gently for two hours with 200 c.c. of water and 15 c.c. of hydrochloric acid of sp. gr. 1.125, whereby starch, dextrin and maltose are converted into dextrose. The dextrose is determined with Fehling's solution after neutralising and diluting to 300 or 500 c.c. If the quantity of dextrose found for 100 g. substance is D_1 , the percentage of starch is calculated as 0.9 ($D_1 - D$).

If the moisture, determined by drying at 110°, is W per cent., and the ash A per cent., the quantity of "other organic compounds" is:— $100 - (\text{maltose} + \text{dextrin} + \text{starch} + W + A)$.

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W. Jettel obtained the following results in several dextrins by this method:—

	Maltose.	Dextrin.	Starch.	Water.	Ash.	Other organic compounds.	Acidity, c.c. N/10 potassium hydroxide.
I.	4.25	47.78	35.55	10.11	0.27	2.04	40.0
II.	10.90	86.75	43.20	7.02	0.39	1.74	26.6
III.	8.75	29.48	58.00	6.85	0.60	1.34	25.3

Undecomposed starch may be detected microscopically and by its insolubility in water. There is generally a small amount of reducing material present from maltose, etc. It may be estimated by Fehling's solution.

It is very difficult to wash dextrin free from starch, and filtration is slow. In any analytical method which involves these operations special precautions must be taken or results are unreliable. A practical method for the determination of dextrin gum has been devised by Babington, Tingle and Watson, which is comparatively rapid and accurate, within 5 per cent. with most commercial samples. The sample (1 g.) is warmed in a 100 c.c. graduated flask with 30 c.c. of water until just gelatinised and then rapidly cooled. Fifty c.c. of a cold saturated solution of barium hydroxide is next added and the volume made up to 100 c.c. Fifty c.c. of the filtered solution is placed in a platinum dish. After the addition of 2 drops of a 1 per cent. phenolphthalein solution, *N/1* hydrochloric acid is added to neutralisation point. A faint pink colour is restored by adding two or three drops of the barium hydroxide solution. Approximately 10 g. of sand is added and the dish heated on a water bath. The sand should be stirred when almost dry, to expose the maximum surface to the air, after which the dish is transferred to a well-regulated oven and dried to constant weight at 120°. The dish is now heated strongly to burn the organic matter completely. The dish is then cooled and weighed. The difference in weight before and after ignition represents the dextrin gum in 50 c.c. of filtrate.

TESTING AND DIFFERENTIATION OF GUM ARABIC, GUM SENEGAL, AND DEXTRIN

Liebermann gives the following procedure for this purpose:—

1. External examination of gum arabic which has not been artificially powdered.

2. External examination of gum senegal.

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3. Both forms of gum are completely soluble in water; only particles of wood remain behind, which are generally reddish in the case of gum arabic, and blackish in the case of gum senegal. These particles of wood are found even in very pure specimens of gum. Other varieties of gum, as, for instance, that of the cherry tree, dissolve only partially in water. A swollen mass remains behind, which dissolves only on prolonged boiling or very long digestion.

4. The aqueous solutions of both sorts of gum give a bluish precipitate with potassium hydroxide and a few drops of copper sulphate; but this is much more pronounced in the case of gum arabic, and collects in large flakes which rise to the surface in the test-tube, whereas the precipitate obtained with gum senegal is less pronounced, and consists of small flocculi, which remain more uniformly distributed throughout the liquid. These precipitates dissolve but slightly on warming, and no reduction occurs even on vigorous boiling.

5. Solutions of dextrin also give bluish precipitates with potassium hydroxide and copper sulphate, which do not dissolve on shaking in the cold, but dissolve completely on heating, giving rise to clear, dark blue liquids. On boiling for some time, complete reduction of the copper oxide occurs.

6. On prolonged heating with dilute potassium hydroxide in a test-tube, solutions of gum arabic and dextrin become amber yellow, whereas solutions of gum senegal are scarcely coloured, or assume only a faint yellow tint.

7. Mixtures of gum arabic and gum senegal behave towards potassium hydroxide and copper sulphate solution in the same way as gum senegal alone; on boiling with potassium hydroxide alone, however, they behave like gum arabic solutions, the liquid becoming amber yellow.

8. Solutions of mixtures consisting of gum-arabic and dextrin behave like gum arabic towards potassium hydroxide and copper sulphate, as regards the appearance of the precipitate. On boiling for some time, however, reduction takes place, if the quantity of dextrin is not too small. The same applies to mixtures of gum senegal and dextrin.

9. If the quantity of dextrin be too small, the reduction may not

take place. In such cases the precipitate obtained with potassium hydroxide and copper sulphate must be filtered off, after moderate warming. The filtrate, which contains no gum, but is still somewhat milky and turbid, is boiled. A distinct separation of red cuprous oxide (or yellow hydroxide) shows the presence of dextrin.

10. The separation must be carried out in the same way, when mixtures of both sorts of gum with dextrin are under investigation. The copper precipitate, containing the acid gum products, is washed with distilled water, dissolved in hydrochloric acid, and this solution

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precipitated with excess of alcohol. The precipitate is allowed to subside for one and a half to two days, the liquid then decanted and the transparent disc of gum, which remains at the bottom of the vessel, washed with alcohol. The small quantity of alcohol remaining behind is allowed to evaporate; or, the gum is dissolved directly in hot water and the aqueous solution tested for gum arabic or gum senegal, as indicated in Nos. 4, 6, and 7.

Lead sub-acetate precipitates gum arabic in aqueous solution. In presence of sugar, addition of alcohol prevents the precipitation of dextrin if the latter is present.

The Examination of Gum Arabic can also be carried out as follows:—

A. Appearance of the gum, according to 1 and 2, if the gum has not been pulverised.

B. Solution of the powdered substance in lukewarm water. Observations as in No. 3. If the substance dissolves only partially, leaving a swollen gelatinous mass, it consists of cherry gum or a similar "gummi nostras," or of a mixture containing such gums. If the substance dissolves, all but a turbidity and a few particles of wood, proceed to:—

C. The aqueous solution is treated with excess of potassium hydroxide and some copper sulphate, gently warmed, and filtered:—

(a) *The Filtrate*, which may contain dextrin, is tested according to No. 9.

(b) *The Precipitate* is examined as in No. 10. If the aqueous solution of gum acids, prepared as described in No. 10, be treated with an excess of potassium hydroxide and some copper sulphate added, a precipitate results, which either agglomerates and rises to the surface, or remains in the form of small flakes uniformly suspended throughout the liquid.

Precipitate Agglomerates.

Gum arabic.

(The aqueous solution becomes amber yellow on treatment with potassium hydroxide.)

Precipitate does not Agglomerate.

Gum senegal, or a mixture of gum senegal and gum arabic.

(The aqueous solution is boiled with potassium hydroxide.)

Amber Yellow
Colour.

No Colour, or Pale
Yellow.

Mixture of gum
arabic and
gum senegal.

Gum senegal.

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In Thevenon's test for gum tragacanth the presence of 5 per cent. gum arabic in gum tragacanth can be observed. A small amount of the mixture is warmed with water and an equal volume of 4 per cent. pyramidon solution added, followed by 10 drops of hydrogen peroxide (12 per cent.). In 5 to 30 minutes a blue colour develops, depending upon the amount of gum arabic in the sample. For quantitative tests a control is done with gum tragacanth of known purity with varying amounts of gum arabic present.

Detection of Gum Substitutes. Many good, strongly adhesive gums have come on the market only in small quantities. As a consequence, substitutes have been exported in large quantities from South America, Australia, etc. Some of these have served the purposes of gum satisfactorily for some technical uses; they proved to be easily soluble, but were all inferior to genuine gum arabic in adhesiveness. Some kinds, however, although of inviting appearance,

proved to be quite insoluble, only swelling up when placed in hot water. It has been pointed out that such gums could be rendered soluble by boiling under high pressure. This is probably correct, but gum so dissolved possesses a very inferior adhesive power, not even equal to that of starch paste; it could therefore be used only for thickening; even in this case starch or tragacanth is greatly preferable.

When such gum substitutes come in the unmixed state into the market, they are easily recognised; but when ground to a coarse powder, and mixed with an equal part of genuine gum gheziri, a simple solution test does not show the presence of substitutes, since the swollen gelatinous particles of the substitute remain suspended, and are completely invisible. In order to detect such adulteration with certainty, the following simple method may be recommended.

The suspected gum is covered with ten times its quantity of hot water, and allowed to stand for three or four hours, with frequent stirring. When the insoluble matter has subsided, half the liquid is poured off, replaced by the same quantity of cold water, and again well stirred. This process is repeated twice within an hour. The last mixture separates after short standing into two parts, the upper layer consisting of water, and the lower layer of a gelatinous, highly refractive mass. In this way, the presence of even 5 per cent. of adulterant can be detected with certainty.

4. Other Adhesives

Among substances which have been suggested as adhesives are (a) casein (B.P. 362001/1930; U.S. Pat. 1886750/1933), (b) rubber

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latex (French Pat. 735348/1932), and (c) Hydroxyalkyl ethers of carbohydrates (B.P. 389534/1933).

E. COLOURING MATTERS

Red lead, manganese dioxide, ochre, umber, smalt, ultramarine, and various coal-tar dyes are employed.

IV. MATERIALS FOR THE STRIKING SURFACE

These are the same as for the match compositions. Manganese dioxide, the sulphides of antimony, powdered charcoal, amorphous phosphorus, potassium chlorate, glass powder, etc., as frictional materials; chalk, etc., as filling materials; umber and the like as colouring matters; glue, gelatin, and dextrin as binding materials.

V. MATCH COMPOSITIONS

A. COMPOSITIONS FOR MATCHES WHICH STRIKE ON ANY SURFACE

This class includes not only matches made with ordinary phosphorus, but also matches free from phosphorus, and those which contain red phosphorus, with or without sulphur and phosphorus sesquisulphide. For a great number of years attempts have been made to eliminate the use of phosphorus, and of special striking surfaces. Many of the proposed substitutes for phosphorus, however, have been too expensive, some too little inflammable, some too unstable, and some only available for paraffined matches.

In those match compositions which contain no white phosphorus, sulphur is mixed with such substances as amorphous phosphorus, phosphorus sesquisulphide, antimony sulphide, thiocyanates, and cyanides of metals, etc.; or, easily inflammable substances, like charcoal, the salts of fatty acids (stearates), carbon compounds, such as naphthalene and phenanthrene, as well as shellac and resins. As oxidising agents, besides those already mentioned, such as potassium permanganate and nitro-compounds, gun-cotton, aromatic nitro-compounds, such as trinitrophenol (picric acid) and picrates, have been tried. These last substances are explosives; their properties are described in the section on Explosives (p. 43). Chlorates and perchlorates have also been used as oxidising agents in match compositions. So as to retard the combustion and to insure a complete ignition of the composition, a small quantity of a complex metallic cyanide, such as

Prussian blue, Turnbull's blue, or even the material used in gas purification, is added; this contains free sulphur, thiocyanates, and complex metallic cyanides.

Rosel gives the following two recipes for the preparation of match compositions:—(1) 10 parts of potassium chlorate, 7 parts of pure and freshly precipitated lead thiosulphate, 2.5 to 2.9 parts of antimony trisulphide, 0.25 parts of gelatin. (2) 300 parts of powdered glass, 120 parts of manganese dioxide, 160 parts of potassium dichromate, and 90 parts of flowers of sulphur; these are mixed together in water and finely ground. In another case 300 parts of gum arabic and 210 parts of glue are dissolved in water, and 1800 parts of well-powdered and sieved potassium chlorate are added; the following substances are then added consecutively, each being finely powdered:—600 parts of lead thiosulphate, 450 parts of red lead, and 25 parts of barium thiosulphate. Rosel gives particulars also of the following composition, containing red phosphorus:—450 parts of potassium chlorate, 100 parts of potassium dichromate, 75 parts of powdered glass, and 60 parts of sulphur (washed flowers of sulphur or powdered roll-sulphur), 25 parts of *caput mortuum* (iron oxide), 7 to 8 parts of red amorphous phosphorus, 110 parts of gum arabic, and 30 parts of gum tragacanth.

Craveri has proposed the use of persulphocyanic acid, which is supposed not to react when hammered or rubbed, is claimed to be non-poisonous and harmless during the manufacture of the match compositions, and cheaper than phosphorus.

The composition made by Bohy, Gallay, & Co., of Nyon, contains salts of hypophosphorous acid, mainly the calcium salt, in place of ordinary or amorphous phosphorus. Calcium, barium, and strontium hypophosphite ignite only at a high temperature; if, however, they are mixed with potassium chlorate or nitrate, or any other oxidising agent, ignition takes place very readily. This composition is made as follows:—210 g. of glue and 30 g. of gum tragacanth are allowed to soften for twelve hours in water, then warmed and boiled; 25 g. of turpentine is added, then 1 kg. of potassium chlorate, 200 g. of sulphur, 150 to 200 g. of a hypophosphite (calcium, barium, or strontium salt), 5 to 10 g. of potassium dichromate, 125 to 150 g. of barium chromate, 200 to 250 g. of powdered glass, and 10 g. of colouring matter. Another composition can be obtained by the further addition of 150 g. of naphthol yellow, or in place of this, 100 g. of picric acid.

Another match composition is made up of barium chlorate, sulphur, inert matter, and a binder, the amount of barium chromate being approximately twice that of the potassium chlorate.

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Even before Sévène and Cahen, Rals had recommended fusing together sulphur and red phosphorus, but the result was not equivalent to phosphorus sesquisulphide. The Sévène-Cahen process was taken up by the French Government, and it is said that the French public did not notice any difference, on the introduction of the so-called "S. and C." matches, containing this substitute for phosphorus.

The "S. and C." composition varies, according to whether it is to be used for paraffined or sulphured splints, or for waxed threads. The ordinary composition is as follows:—6 parts of phosphorus sesquisulphide, 24 parts of potassium chlorate, 6 parts of zinc oxide (zinc white), 6 parts of red ochre, 6 parts of powdered glass, 6 parts of glue, and 34 parts of water. It is easy, by manipulation, to make these matches either more or less inflammable. The mechanical processes are much the same as in the manufacture of phosphorous matches.

In Aronson's composition a small proportion of potassium oxy-salts are used with a relatively large proportion of phosphorus mixed with an equal proportion of lamp-black or other non-glowing material, and binding agent (dextrin).

The Chemische Fabrik Griesheim-Elektron has placed on the market a product, called "Sulfophosphit," which consists of zinc, phosphorus, and sulphur. It is stated that both paraffined and sulphured matches can be made with this substance, with any required degree of inflammability. "Sulfophosphit" is claimed to be more stable, under atmospheric influences, than red phosphorus and phos-

phorus sesquisulphide; also, the price is alleged to be low.

The basis of another dipping composition, made by R. Gans, is a mixture of "sulfocuprobaryumpolythionate" and potassium chlorate. The composition is said to be comparatively insensitive to warmth, and to keep for a long time. The splints, after dipping, are coated with a spirit or water varnish. This new composition is said to be more inflammable than that of Schwiening.

B. COMPOSITIONS FOR SAFETY MATCHES WHICH REQUIRE A SPECIAL STRIKING SURFACE

Brown Safety Match Composition (Kellner). One hundred and fifty parts of gum senegal are dissolved in 200 parts of water, and at the same time 20 parts of powdered tragacanth are digested in 300 parts of water for twenty-four hours; these solutions are united and boiled, and 100 parts of powdered and sifted potassium chlorate introduced. To

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this is added a finely powdered and thoroughly mixed mixture of 125 parts of potassium dichromate, 30 parts of sulphur (crushed roll-sulphur or washed flowers of sulphur), 33 parts of antimony trisulphide, 50 parts of powdered colophony, 200 parts of minium or of lead peroxide 100 parts of umber or terra di Sienna, 100 parts of powdered glass or powdered pumice stone, and lastly 150 parts of hot water.

Composition for the Striking Surface.—Four hundred parts of dextrin are mixed with 400 parts of water, boiled, and allowed to cool; with this is mixed a thin paste of red phosphorus, which has been made by stirring 1000 parts of red phosphorus with 2000 parts of water, allowing to stand, and pouring off the excess of water. Then 200 parts of prepared chalk (the mass swells up, owing to evolution of carbon dioxide), 300 parts of umber, and 1000 parts of finest powdered antimony sulphide are added, and the whole mixture passed through a mill.

Rossel used the following composition:—Ten parts of gum arabic, 300 parts of gum tragacanth, 53.8 parts of potassium chlorate, 6 parts of *caput mortuum*, 12 parts of powdered glass, 5 parts of potassium dichromate, 3 parts of sulphur, 1.2 parts of chalk or colophony, and 6 parts of manganese dioxide. The striking surface for this composition consisted of 5 parts of antimony sulphide, 3 parts of amorphous phosphorus, 1½ parts of manganese dioxide, and 4 parts of glue.

Moisture-proof striking surfaces are formed by mixing the active substances with a solution in an organic solvent of a hardening insoluble non-combustible binding agent.²

A phosphorus-free striking surface, recommended by Craveri,³ on which any safety-match will ignite, is made up as follows:—Two parts of a thiocyanate compound, 1 part of persulphocyanic acid, 0.5 parts of potassium xanthate, 4 parts of antimony sulphide, and as a binding material, 1 part of gelatin.

Many different types of matches or match substitutes have been suggested from time to time, but they have not come into general use. As one example of this type, reference may be made to "rods" capable of ignition by friction.⁴ The rods can be extinguished and re-ignited repeatedly. They comprise a foundation of organic substances, ash free and having a speed of combustion less than that of a low nitrated cellulose. A typical mixture of this class consists of cellulose nitrate or acetate mixed with ammonium oxalate, camphor, or naphthalene and an ignition mixture free from phosphorus (e.g. potassium chlorate and sulphur). Additional substances, as binders, combustion regulators, filters, pigments, etc., may also be added.

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VI.—THE CHEMICAL EXAMINATION OF MATCH COMPOSITIONS

The composition, when examined under the magnifying glass, should be as uniform as possible, and it is important that no particles of phosphorus should be visible.

The following method of examination is recommended by Bolley, for the purpose of determining the constituents of a match composition. The matches are placed in water at a maximum temperature of 20°, in a porcelain basin, the swollen heads removed by mechanical means, and

after having been broken up under the water, digested and continually stirred (in the absence of phosphorus, the mixture can be boiled), and then separated by filtration.

1. The filtrate, which may contain potassium chlorate, potassium nitrate, lead nitrate, potassium chromate, potassium ferrocyanide, gum, glue, and dextrin, as well as other substances that are soluble in water, is divided into several portions. One of these is tested for lead, another for chlorate. Another portion is evaporated and ignited; if the residue, on moistening, gives an alkaline reaction, a nitrate is present. Ferrocyanic acid is tested for with a ferric salt. To determine the presence of gum or glue, a rather larger portion of the same filtrate is evaporated to dryness with sodium hydroxide; on heating a portion of this residue in a tube, the presence of glue or albuminous matter is indicated by the evolution of ammonia gas, which can be tested for in the usual manner, either by smell, or with hydrochloric acid, or with turmeric paper. Gum and glue are precipitated from the solution on addition of alcohol. The presence of dextrin in the solution is determined by the addition of a few drops of a solution of iodine, when a pale reddish-blue coloration is formed.

2. The residue on the filter paper is digested with alcohol, so as to extract stearic acid, paraffin, and resins. To extract wax, it is necessary to boil with the alcohol; this is not permissible, however, in the presence of phosphorus. The alcoholic filtrate, after evaporation, yields a substance, from the consistency, melting point, etc. (solubility in ether, fractional crystallisation, and melting point), of which conclusions can be drawn as to the nature of the residue. If phosphorus is present in the residue it can be removed before the digestion with alcohol, by treatment with nitric acid to convert it into phosphoric acid, which is recognisable by the usual means.

Matches containing phosphorus become luminescent in the dark, and when moistened with water, give the characteristic smell of phosphorus.

3. The original residue, which remains after the digestion with water, will evolve chlorine on heating with hydrochloric acid, if lead

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peroxide, red lead, or manganese dioxide be present; the smell of sulphurous acid denotes sulphites, and lead, manganese, iron, and antimony can be tested for in the residual solution. The presence of lead peroxide, or of red lead, is recognised from the colour of the match-head. Ochre remains partly, and smalt completely, undissolved; both can be recognised with the blowpipe, whereas ultramarine is decomposed by hydrochloric acid, evolving sulphuretted hydrogen. Charcoal, sand, and powdered glass remain undissolved in hydrochloric acid, and can be identified with a magnifying glass; sulphur can be recognised by its colour, by the smell on burning, or it can be extracted with carbon disulphide.

A. EXAMINATION FOR PHOSPHORUS

The recognition of phosphorus is very much simplified by its luminosity in the dark; but with a small quantity of phosphorus in a very large quantity of matter, for instance, in poisoning cases, either in a quantity of food, or in the stomach contents, this luminescence does not show, even when friction is applied. The material is firstly examined for an odour of phosphuretted hydrogen or of ozone, which would denote the presence of free phosphorus. It should be examined by Scherer's test as follows:—Strips of paper, soaked respectively in a 5 per cent. silver salt solution and in an alkaline lead solution (5 per cent.), are hung up over the material for examination. If phosphorus is present, the silver paper only will be blackened; should both papers turn black, the presence of sulphuretted hydrogen is proved, but not the presence of phosphorus; that is to say, this test for phosphorus fails in the presence of sulphuretted hydrogen. Even when a positive test is obtained the results must be confirmed otherwise, preferably by Mitscherlich's test. Attempts can also be made, by treating the matter with water, to collect any minute floating particles of phosphorus in a filter, and if this is successful, they can be oxidised by nitric acid to phosphoric acid and tested for in the usual way. The material may also be treated

with a small amount of benzene and a strip of paper 10 cm. by 3 cm. soaked in it. This is then suspended in a glass tube connected to a Victor Meyer's heating apparatus and exposed to a current of air at 40° to 50° . Even when the benzene solution contains not more than 0.01 mg. of white phosphorus per c.c. the paper will become luminescent when examined in the dark.

The following method, however, due to Mitscherlich, is satisfactory:—The mass is acidified with sulphuric acid, and distilled with steam, the vapours being passed through a vertical condenser; if

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phosphorus is present, it is vaporised with the steam, and can be recognised as a luminescent ring, which moves up and down in the condenser. The test is conducted in a darkened room; it is possible by this means to detect 0.00001 parts of phosphorus. It is often possible to find small particles of phosphorus in the distillate, and to obtain the test for phosphorous acid. The phosphorus and phosphorous acid are treated separately with strong chlorine water, and thus oxidised to phosphoric acid, which is estimated in the usual manner with magnesia mixture, as ammonium magnesium phosphate.

Care must be taken in carrying out this test that alcohol and ether, should they be present, do not prevent the luminescence of the vapours. Turpentine and other volatile oils, as well as phenol and creosote, often completely prevent it; furthermore, red phosphorus does not produce this luminescence, but mixtures of sulphur and phosphorus, such as are found in match-heads, will cause it. According to Polstorff and Mensching, the luminescence is also hindered by the presence of mercury salts. Copper salts and sulphuretted hydrogen also are said to interfere. Even after continued distillation, the whole of the phosphorus will not be found in the distillate; O. Schifferdecker calculates that for every milligram of phosphorus in the distillate, the original substance contained 1.5 to 2.0 mg.

According to K. Fischer, the presence of potassium chlorate in match compositions greatly interferes with the testing for phosphorus, and it is advisable to wash the sample several times with cold water to eliminate the chlorate, before distilling. If substances soluble in water are to be determined, the two tests can be combined. The washing with water can be avoided by using tartaric acid for the distillation instead of sulphuric acid; the presence of potassium chlorate does not then influence the phosphorus test.

Another means of detecting phosphorus, described by Dusart and Bloudot, is based on the fact that small quantities of phosphorus, phosphorous acid and silver phosphide, give with nascent hydrogen, phosphuretted hydrogen, which can be recognised by the emerald green colour imparted to the hydrogen flame when a porcelain basin is held in it. The hydrogen must be free from sulphuretted hydrogen, and must be passed through a tube containing pumice-stone soaked in potassium hydroxide, before lighting, otherwise the flame would appear blue; the gas exit tube should have a platinum-covered tip, as the sodium contents of the glass will otherwise colour the flame. The substances containing phosphorus must not be introduced directly

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into the hydrogen-generating mixture, as they easily prevent the formation of the green flame. But the phosphorous acid or phosphorus particles obtained by Mitscherlich's test, can be introduced into a suitable mixture of zinc and dilute sulphuric acid; or silver phosphide, which is obtained as a black powder by heating the acidified phosphorus-containing matter in a current of carbon dioxide, and passing the gas into a solution of silver nitrate, may be so introduced. The green flame appears in the presence of the smallest trace of phosphorus, and, according to Christoffe and Beilstein, gives a spectrum with three green lines, of which the two strongest are in the green, and the weakest in the yellow. Dusart's test has been modified by Dalmon in such a manner that the whole of the organic matter containing phosphorus is treated with hydrogen. The gas is passed through a long drawn-out glass tube, bent upwards at right angles, and is lighted at the end; if a narrow glass tube is pushed over the jet, the flame shortens, and appears green, for the whole length of the tube, and when

the tube is pushed down further, the flame shortens still more, becomes dark blue, and if the glass tube is slowly drawn away at this moment, a magnificent emerald-green flame-ring appears, passing up the tube with greater or less velocity. The phosphorus-charged hydrogen, generated in this way, luminesces in a dark room, without the gas being ignited.

In Schloesing's test for free white phosphorus in phosphorus sesquisulphide the latter is shaken with light petroleum (b. pt. 45°) to dissolve free phosphorus. The liquid is quickly filtered and an aliquot part evaporated in a vacuum at 15° to 20° . The residue is oxidised with nitric acid and the phosphorus estimated. In order simply to detect the presence of phosphorus, the residue after evaporating off the petroleum is shaken with fine sand in a flask in the dark and carefully examined for phosphorescent glow.

With regard to the period during which phosphorus will remain in organic matter and can be tested for, Medicus gives the following data:—Neumann found phosphorus in a corpse after it had been buried for fourteen days. Dragendorff mentions a case, in which he was able to detect phosphorus in the secretions in a corpse that had been buried for several weeks and afterwards exhumed. Fischer and Müller were able to detect phosphorus in the body of a guinea-pig, which had been buried for eight weeks. On the other hand, Herapath was unable to detect a trace of phosphorus twenty-three days after

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death; Brandes could find no phosphorus in the corpse of a child after three weeks, but could detect its acids. Medicus was able to detect phosphorus for half an hour by Mitscherlich's test twenty-three days after poisoning; the sulphuric acid solution, after filtering, gave a gas containing phosphorus on treatment with zinc and hydrochloric acid.

B. TESTING FOR ORDINARY PHOSPHORUS IN MATCH-HEADS

Prohibition of the Use of White Phosphorus.—Subsequent to conferences held at Berne in 1905-6, certain European countries discontinued the use of white phosphorus in the manufacture of matches. In Germany a law that white phosphorus should cease to be used for the manufacture of matches after 1st January 1907 was approved. In the United Kingdom the "White Phosphorus Matches Prohibition Act (8 Edward VII., 1908, chapter 42)" was passed on 21st December 1908, and came into force on 1st January 1910. According to this Act:—"It shall not be lawful for any person to use white phosphorus in the manufacture of matches, and any factory in which white phosphorus is so used shall be deemed to be a factory not kept in conformity with the Factory and Workshop Act, 1901. . . . It shall not be lawful for any person to sell or to offer or expose for sale . . . any matches made with white phosphorus. . . . It shall not be lawful to import into the United Kingdom matches made with white phosphorus, and matches so made shall be included among the goods enumerated and described in the table of prohibitions and restrictions contained in section 42 of the Customs Consolidated Act, 1876."

Detection of White Phosphorus.—It is now necessary, therefore, to test for white phosphorus in match-heads, in cases where its presence is suspected. Hitherto no exact method has been advanced, suitable for the detection of white phosphorus under all conditions.

On the one hand, the examination of phosphorus sesquisulphide, which is frequently present, is, according to Friedheim, difficult, because the sulphur-phosphorus compounds gradually decompose into compounds containing less sulphur, with separation of white phosphorus, and on the other hand, the detection of phosphorus in matches in presence of potassium chlorate cannot be carried out by the ordinary methods of analysis.

In some cases it is possible, when examining match-heads stated to contain no white phosphorus, and to which no white phosphorus has been added as such, to demonstrate the presence of this substance, yet it cannot be ascertained whether it was added, or whether it was

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re-formed from phosphorus sesquisulphide. Again, in other cases, no

phosphorus may be detectable, notwithstanding its presence, because the test sometimes fails in presence of potassium chlorate (*cf.* p. 135).

To test for ordinary phosphorus, at least twenty-five match-heads are placed directly in a Mitscherlich apparatus, with 50 c.c. of water and 10 c.c. of dilute sulphuric acid. The mixture is heated over a flame, without the introduction of steam (*cf.* p. 134); if potassium chlorate is present, the phosphorescence may not appear (*cf.* p. 135); but on the other hand, phosphorus sulphide is capable of producing a luminescence which, though different from that caused by phosphorus, may be mistaken for it. In the first case, either the substances soluble in water, including the potassium chlorate, must first be removed from the match-heads with cold water, or the test must be carried out with tartaric acid. To determine the presence of very small amounts of yellow phosphorus in red phosphorus the following test has been proposed by Kray :—

20 g. of the red phosphorus product is dissolved in 30 c.c. of carbon disulphide and filtered. Part of the filtrate is tested with filter paper which has been impregnated with copper sulphate solution; the depth of the brown colour is a measure of the amount of yellow phosphorus present.

To test for ordinary phosphorus in the presence of phosphorus sulphide (phosphorus sesquisulphide, P_4S_3), the following process, due to R. Schenck and E. Scharff, can be employed. This method is based on the property of ordinary phosphorus, when oxidised to phosphorus trioxide, of ionising the air, which then becomes capable of conducting electricity. Phosphorus and sulphur compounds, even if they luminesce, do not produce this effect.

The apparatus employed (*Fig. 9*) consists of two parts, connected by a glass tube, viz., the vessel *a*, for generating the phosphorised air, and the electroscope *b*. The former is a test-tube with a side connection, and a ground glass stopper, through which the air delivery tube passes, reaching nearly to the bottom of the test-tube. A glass tube is attached to the side connection by means of rubber tubing, which delivers the phosphorised air to the cylindrical condenser *c*, the removable top *d* of which carries the electroscope. Within the outer cylinder *c* is an insulated cylindrical disperser (*zerstreuungskörper*) suspended from the electroscope.

The phosphorus oxidation products are prevented from entering the inside of the electroscope case *b*, from *c*, by two insulated plates, which can be removed and cleaned, and through which the carrier of

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the disperser passes and fits closely. A small piece of sodium is put in *c* to prevent access of moisture. A rod, by means of which the disperser can be charged, which is well insulated and has a properly insulated handle, passes through the lid of the cylinder *c*.

To charge the electroscope, the rod is pushed down close to the disperser, and Zamboni's dry pile brought up to it and then removed; after charging, that is, when the aluminium leaves of the electroscope

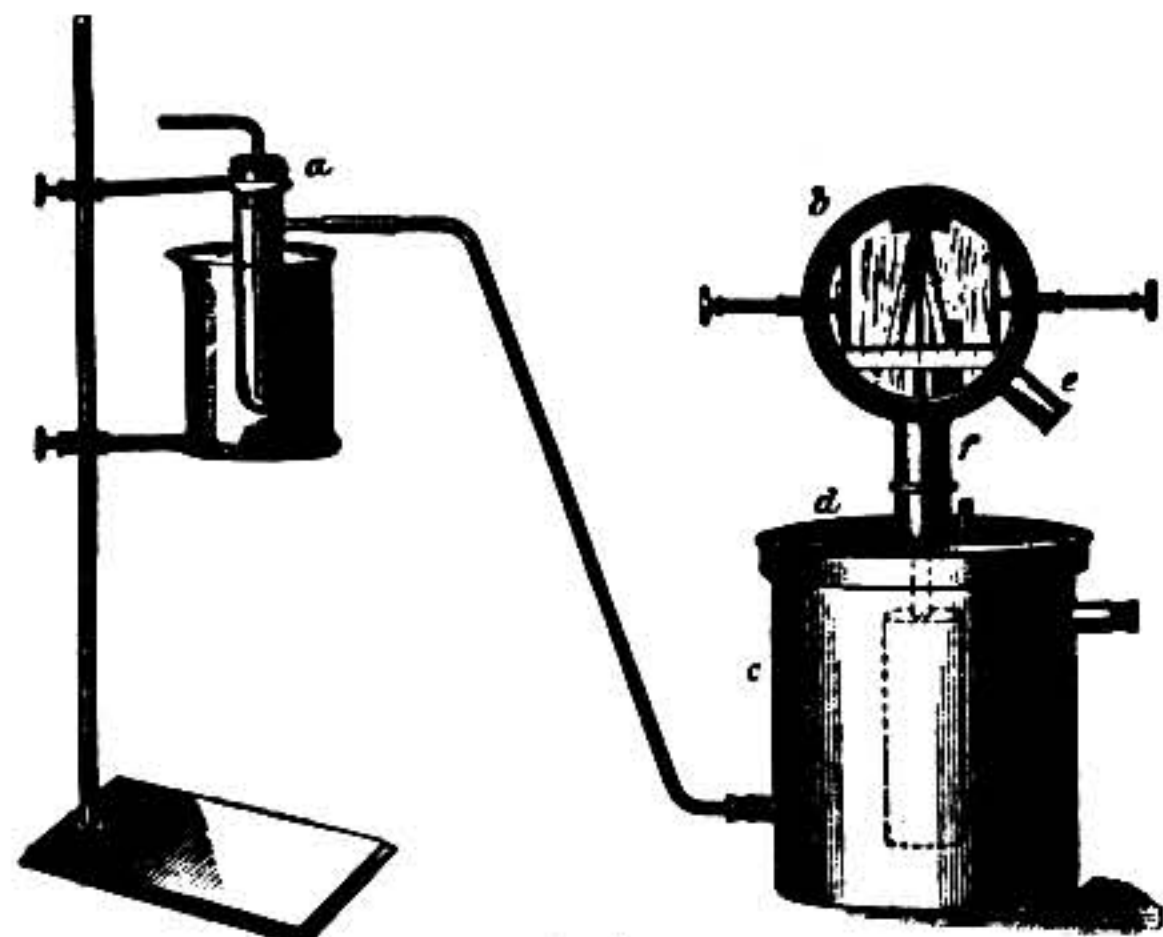


FIG. 9.

are apart, the rod is drawn up again.

To carry out the test, some of the match composition, for instance a few softened and ground match-heads, mixed with zinc oxide (to hold back sulphuretted hydrogen), are placed in the test-tube *a*, which is surrounded by warm water at 50°; after the electroscope has been charged, air is blown through about ten times successively with the aid of a rubber ball, or the air can be drawn through by connecting an aspirator, care being taken to place a bottle of several litres capacity, to catch any solid matter that might get sucked over, between the aspirator and *c*.

In the presence of the smallest quantities of ordinary phosphorus, the electroscope will be discharged, that is to say, the aluminium leaves fall together suddenly. Under normal conditions this takes place only slowly. The leaves ordinarily move through 0.2 to 0.5 divisions of the scale in five minutes.

The following method for the detection of white phosphorus in matches is based upon that of Aronstein. One hundred or more

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match-heads are moistened with water, and then boiled with carbon disulphide for two hours under a reflux condenser. The cooled extract is filtered through a dry filter paper into another flask, and the carbon disulphide distilled off on a water bath. The flask containing the residue is at once connected with an apparatus by which, firstly, carbon dioxide, and secondly, dry air can be introduced. While the current of carbon dioxide is driving off the small quantity of carbon disulphide remaining in the flask, the temperature of the water in which the flask is immersed is gradually raised from about 15° to 30°. The room having been previously darkened, dry air is admitted into the flask at different and increasing temperatures, the current of carbon dioxide meanwhile being almost entirely turned off. Careful watch is kept for any sign of luminescence. If there be none at 30°, the temperature is gradually raised. In most cases, when white phosphorus is present, luminescence is seen below 35°; very occasionally it may first appear at as high a temperature as 55°. The glow temperatures observed in two experiments (December 1910), with matches containing white phosphorus, were 23° and 25° (E. G. Clayton). The lowest limit of glow for phosphorus sesquisulphide, in the absence of white phosphorus, is generally about 60°, so that this process can be applied to the detection of small quantities of white phosphorus in the presence of considerable amounts of phosphorus sesquisulphide.

According to C. Van Eijk,² a tube containing phosphorus sesquisulphide is not luminescent below 70°, but if 0.02 per cent. of white phosphorus be present a glow appears below 60°. An alternative plan is to extract with carbon disulphide, evaporate off the solvent, and distil the residue with a solution of lead acetate. Sesquisulphide of phosphorus is decomposed, and luminescence appears only in the presence of white phosphorus.

T. E. Thorpe's Sublimation Test for white phosphorus is carried out as follows :—A few grams of the match-heads, or of the composition, are dried thoroughly over sulphuric acid in a desiccator filled with carbon dioxide, and transferred to a bulb of 25 c.c. capacity blown on the end of a tube 20 cm. long and 15 mm. in diameter. Dry carbon dioxide is introduced, the apparatus evacuated as completely as possible, and the end sealed off. The bulb is then gently heated for two hours at from 40° to 60°. Phosphorus, if present, will be volatilised, and condensed in the upper part of the tube as a transparent, highly refractive sublimate of octahedral or dodecahedral crystals. It is claimed that this is the most trustworthy test for the presence of small quantities of ordinary phosphorus in the striking compositions of matches containing phosphorus sesquisulphide.

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The test of Phelps is more sensitive than the above for small quantities of phosphorus, and it is more rapid when a large number of samples require examination. It is based on the volatility of white phosphorus in a current of steam and its luminescence with oxygen. 0.1 mg. in 10 c.c. of water can be detected. Hydrogen after washing

with alkaline pyrogallol is passed into boiling water containing ten to twelve match-heads. The gas issues through a fine capillary at a relatively high velocity. The capillary is enclosed in a dark chamber and is viewed through a small microscope. The upper two inches of the capillary are heated electrically to prevent condensation. The method is applicable in the presence of nitrates, chlorates, hydrogen sulphide (phosphorus sesquisulphide), or carbon disulphide.

C. TESTS FOR CYANOGEN COMPOUNDS

When soluble cyanides or ferro- and ferri-cyanides are distilled in the presence of potassium chlorate, with sulphuric acid, free hydrocyanic acid is found in the distillate; insoluble substances of this nature, such as Prussian and Turnbull's blue, and "the spent oxide" of gasworks also are decomposed. Accordingly, when testing for cyanogen compounds, 1 g. of the scraped match-heads is treated with 50 c.c. of warm water and filtered, and both the filtrate and the residue distilled separately with dilute sulphuric acid. Hydrocyanic acid can be identified in the distillate by the following reactions:—

1. *Prussian Blue Reaction.* To the distillate is added a drop of ferric chloride and a drop of ferrous sulphate solution, or only a drop of ferrous sulphate solution, as this generally contains a little of the ferric salt; this is then made alkaline with a little sodium or potassium hydroxide, well shaken and carefully acidified with hydrochloric acid. In the presence of hydrocyanic acid, a precipitate of Prussian blue is formed, or the liquid turns green and deposits blue flakes on standing.

2. *Thiocyanate Reaction (Liebig).* Another portion of the filtrate is evaporated on the steam bath with sodium or potassium hydroxide and a little yellow ammonium sulphide; any hydrocyanic acid present is converted into sodium or potassium thiocyanate, which, when taken up with water and a little hydrochloric acid, gives a deep blood-red coloration on the addition of a drop of ferric chloride.

3. *Nitroprusside Reaction (Vortmann *).* To another portion of the distillate a few drops of potassium nitrite are added, then two to four drops of ferric chloride, and enough dilute sulphuric acid to convert the yellow-brown colour into pale yellow. The liquid is heated until it just begins to boil, cooled, a little ammonia added (enough to precipitate

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the excess of iron), and filtered. Two drops of dilute, colourless, ammonium sulphide are then added to the filtrate; a violet coloration, changing to blue, green, and yellow, shows the presence of hydrocyanic acid. Very small quantities give only a bluish-green or a greenish-yellow coloration. This reaction is the reverse of the well-known nitroprusside test for sulphuretted hydrogen and alkali sulphides, and is based on the conversion of any cyanogen present into potassium nitroprusside, $K_2Fe(NO)(CN)_6$, which is a very delicate reagent for alkali sulphides.

4. *Silver Nitrate Reaction.* The distillate is treated with nitric acid and silver nitrate; the presence of hydrocyanic acid is shown by a white precipitate, which should be stable to the light, and readily soluble in ammonia and potassium hydroxide.

D. QUANTITATIVE ANALYSIS OF MATCH COMPOSITIONS

The composition, without any previous softening with water, is carefully separated from the splints, with a sharp knife, care being taken to remove as little wood as possible, and weighed. Or the weight of the head can be estimated by drying several cut-off match-heads in a desiccator over sulphuric acid, and weighing them, then removing the heads with warm water, and drying and re-weighing the pieces of wood.

The estimation of free white phosphorus is carried out, as described on p. 137, and that of the other constituents by the usual methods. For the estimation of potassium chlorate, 0.5 g. of the composition is washed several times with 50 c.c. of water, a little potassium iodide (free from iodine) added, and one and a half times the volume of fuming hydrochloric acid. The whole is heated in a closed bottle for fifteen to twenty minutes on the steam bath, and when cold, the liberated iodine titrated with *N/10* sodium thiosulphate.

VII. PHYSICAL TESTS

A. INFLAMMABILITY ON STRIKING SURFACES

Swedish and other safety-matches are supposed to strike only on the prepared surfaces on their boxes, but as a matter of fact they will ignite on several striking surfaces, such as hard wood, smooth hard paper, fine grained and not quite smooth stones, glass, porcelain, etc.

For tests carried out in Germany, the following materials were used:—A smooth board of beech wood 40 cm. long, a sheet of glass 40 cm. long, hard paper, the width of a match-box striking surface, 10 cm. and 20 cm. long, a fine grained plate of marble 15 cm. long, a

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slightly rough iron plate 15 cm. long, rough glass paper 5 cm. long, and fine grained glass paper 10 cm. long. To apply the test, the match is drawn with an even, gentle pressure slowly over the surface.

B. TEMPERATURE OF IGNITION

To ascertain the exact temperature at which matches will ignite is extremely difficult, on account of the various necessary precautions, and because concordant results are not obtained when the work is carried out under the same conditions. The temperature at which they will inflame of their own accord, in the case of white phosphorus matches, for instance, is lower as the percentage of phosphorus rises, and is more or less dependent on the distribution of the phosphorus in the composition. The more evenly the phosphorus is distributed throughout the composition, the higher will be the temperature of ignition; should a match-head contain a fairly large piece of phosphorus, it is possible for the temperature of ignition to be very little above that of phosphorus. On the other hand, it is known that, by continued careful heating in a current of air at about 70°, many kinds of matches lose their phosphorus, so that although the matches keep their shape and appearance, they are either almost unignitable or the temperature of ignition is found to be much higher than the real ignition temperature. Moreover, the better the matches have been varnished, the higher the temperature of ignition. The ignition point of badly varnished matches varies with the thickness of the coating. The temperature of ignition of any one class of goods can accordingly vary with the circumstances and the methods employed. A large number of tests should therefore be made, and an opinion given with very great care.

The apparatus used in Germany consists of a double-walled, asbestos-covered aluminium box with a double-walled door, provided with a small pane of mica for the purpose of observation. It is provided with three tubes for thermometers, and for inserting the matches, which can be placed at any height inside the box. The apparatus is divided longitudinally inside into three sections by pieces of wire gauze, in the central one of which is placed the thermometer, and in the side ones the matches for testing. The wire gauze serves to protect the thermometer, as well as the neighbouring matches, from pieces of match composition which may fly off from matches which ignite at a lower temperature. The apparatus is heated by a regulated rose-burner.

Another form of apparatus consists of a glass vessel with a copper lid, in which four springs are arranged for carrying test-tubes. The thermometer can be inserted in the centre of the lid. The vessel is filled to about one-third with pure liquid paraffin. A copper wire

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stirrer passes through the lid. The matches to be tested are hung on the ends of copper wires in the test-tubes.

This apparatus is similar to that described for explosives (*cf.* p. 71 of this Vol.).

In testing sulphur matches and wax matches, the sulphur or wax should first be removed, as the wax in every test, and the sulphur when the temperature became too high, would melt, and enclose the match-head.

The determination of the ignition temperature can also be carried out by the method devised by Leyque and Champion. A copper rod, which is to be heated at one end, has at the other end indentations, 10

cm. apart; these concavities or holes are filled with oil or with d'Arcet's alloy (sometimes called Newton's alloy), consisting of 8 parts of bismuth, 5 parts of lead, and 3 parts of tin, and melting at 94.5° . The rod is provided with six holes, and has a length of about 70 cm. from the first hole. Thermometers are inserted in the holes, and that point on the rod is found at which the match composition will ignite.

C. BEHAVIOUR UNDER PERCUSSION

K. Fischer recommends a method by which the results can be expressed in figures. He uses a striking apparatus, consisting of an oak block, partly filled with lead, and protected beneath by an iron plate; this runs in two iron grooves, from a height that can be varied, and falls on to an iron plate on which the match is placed. The height of fall, multiplied by the weight of the block, gives the force necessary to ignite the match in kilogram-metres. The height of fall is 1 metre; the weight of the block can be increased as desired by addition of lead. The greatest weight of the block is 1.5 kg., so that the largest amount of work which the machine can do is 1.5 kg.-metres. The results are not very accurate, as several circumstances, friction, for example, are not taken into account. However, as these errors are the same in each test, the results are comparative. The sensitiveness of one and the same class of matches under percussion varies very widely. Matches

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of the same class with large heads ignite more readily than those with small heads. In general, the scraped-off composition is more easily ignited than the match, so that in forming conclusions from this test as much care must be exercised as in judging the temperature of ignition. For a general review of the influence of shock on explosive materials see *Przemysl. Chem.*, 1936, 20, 117; *Chem. Abstr.*, 1937, 31, 2435.

D. SENSITIVENESS TO MOIST AIR

To test this property the matches are placed in a vessel over wet cotton wool, and the vessel then placed under a bell jar over a vessel of water. Observations are made with regard to the behaviour of the matches when moist, their durability, appearance, stickiness, and the like.

E. BEHAVIOUR WHEN TREATED WITH CONCENTRATED SULPHURIC ACID BY MOISTENING OR BY IMMERSION

Observations are made as to whether inflammation of the match-head takes place with this treatment.

B. PRIMINGS AND FIREWORKS

Fireworks, so far as their active contents are concerned, are derived from a comparatively small number of components or mixtures (fire-work mixtures).

These comprise, on the one hand, easily combustible substances, such as charcoal, sulphur, antimony sulphide, resins, and tar; and on the other hand, they include substances which readily give up oxygen and support combustion, such as saltpetre (potassium nitrate), and potassium chlorate or other chlorates. A third category includes those substances used for the various colour effects (barium, strontium, copper, and other salts), and also finely divided metals, and coarse particles of charcoal, to cause sparks and showers of fire ("golden rain," and the like). Other substances are sometimes used to decrease the rate of burning and to increase brilliance (e.g. mercurous chloride and mercuric thiocyanate).

I. FIREWORK COMPOSITIONS

The following substances form the groundwork of most firework compositions:—Gun-powder (grain powder and meal powder), saltpetre and sulphur, charcoal mixture, and grey mixture.

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A. GUN-POWDER

Ordinary coarse-grained gun-powder (grain powder) is used for

impulsive or percussive charges (for throwing fireworks from bombs, mortars, etc.), or for explosions; the coarse-grained powder is necessary in these cases as quick combustion and a rapid evolution of gas are required.

Further, meal powder, that is, a finely powdered blasting powder, is used; that employed by makers of fireworks is of varying composition. For instance, a blasting powder is used, which, powdered and passed through a 0.5 mm. mesh sieve, consists of:—

60.2	parts by weight of doubly refined potassium nitrate.
18.4	" " of sulphur,
21.4	" " of alder wood charcoal,

and explodes at 20° by Wagner's powder test.

An ordinary blasting powder, consisting of 70 parts of saltpetre,

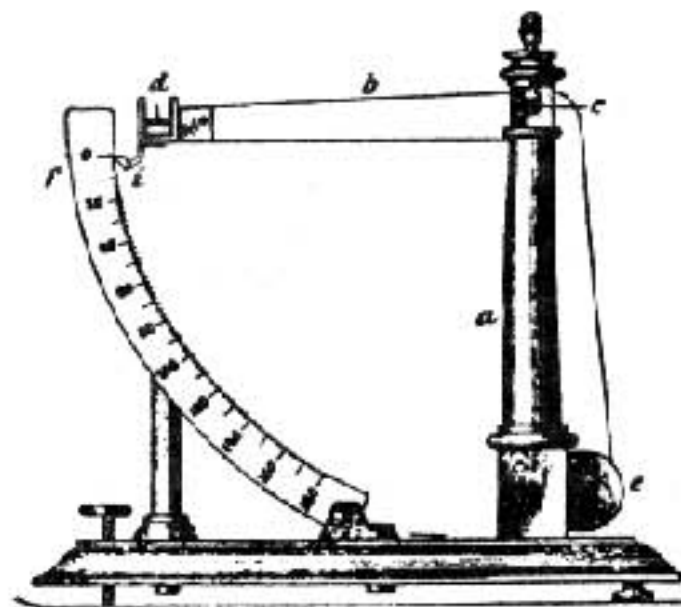


FIG. 10.

18 parts of sulphur, and 12 parts of charcoal is suitable. As a matter of fact, any ordinary gun-powder can be converted into meal powder, as its strength can easily be modified by the proportions of the ingredients. Meal powder is used when slow combustion is necessary. The qualitative and quantitative tests are carried out as detailed under Gun-powder (p. 29).

Wagner's Powder Test. In various factories, where fireworks are made, it is necessary, for some of the mixtures and for the calibre of the cartridges, to use a gun-powder of definite power. Tests by which the power can be estimated are carried out by means of Wagner's apparatus.

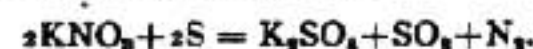
This apparatus (Fig. 10) consists of a column *a*, fastened to a

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support, which can be levelled by means of screws; *b* is an angular lever, which moves on a hinge at *c*, and carries the counter-weight *e*. The unweighted arm *b* carries a small mortar *d* and a spring catch *i*, which moves over a graduated metal arc *f*. When the powder explodes, the arm is pressed downwards by the force of the explosion, and the distance through which it is displaced is shown by the spring catch. The number of degrees can be read directly from the graduated scale. The charge for each test is 2.2 g. of powder. The results obtained by this method are not very accurate, owing to the large size of the mortar, and the smallness of the charge; it is therefore necessary to repeat the test several times, and to take the mean of the results.

B. SALTPETRE AND SULPHUR

This is a mixture of 3 parts of nitre with 1 part of sulphur, and contains approximately equivalent weights of the two components. When this mixture, which yields very little gas, is burnt, the products formed are mainly potassium sulphate, sulphur dioxide, and nitrogen, in accordance with the following equation:—



This mixture is the basis for most compositions which are to give light, and also for grey mixture.

C. GREY MIXTURE

This is made by mixing 7 parts of meal powder with 100 parts of

saltpetre and sulphur, and is mostly used for the manufacture of fire-balls (used in war). These consist of twill bags, charged with compressed grey mixture, which is filled into them with the aid of spirit; they are fired by means of a composition fuse. Grey mixture mixed with antimony sulphide is used for torches.

This material can be tested in the same manner as gun-powder (p. 29).

D. CHARCOAL MIXTURE

This name is given to meal powder, of which 500 parts are mixed with 6 to 8 parts of charcoal. To this class also belong the slow mixtures or slow fires, which consist of meal powder, the explosion of which is more or less retarded by additions of charcoal. Further, there are quick and slow squib mixtures, also so-called "green" mixtures, which are made up of various kinds of slow mixtures. The green mixtures contain larger proportions of sulphur. In addition there are propelling mixtures, which consist of meal powder, nitre, and charcoal (sometimes a little chlorate of potash), and spark mixtures, similar to

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the last, consisting of nitre, sulphur, and charcoal. The former are used for war rockets, and the latter for firework rockets. It is necessary that these mixtures should evolve large quantities of gas, and they are therefore made with a meal powder to which charcoal has been added. An old Prussian prescription for war rockets is as follows:—Thirty-two parts of nitre, 12 parts of sulphur, 32 parts of meal powder, and 16 parts of well-powdered charcoal.

Hence it is apparent that the charcoal mixture can be used, as these are very similar to the spark mixtures which consist of:—

Nitre	12 or 16 parts
Sulphur	3 or 4 "
Charcoal (coarse)	5 or 9 "

Spark mixtures are used for cases, constricted at one end, which can be suitably grouped and mounted, so as to be used for cascades of fire, suns, fans, palm trees, fixed stars, and various other kinds of fireworks. These mixtures are also made up with additions giving a reddish light, and with metal filings; those containing metals are known as "brilliant mixtures."

Finely divided metals, such as aluminium or magnesium, with various oxygen-containing substances, may be used for flashlights. Krebs uses zirconium with the nitrate and barium nitrate or other oxidant.

Such mixtures are analysed similarly to gun-powder. For tests for potassium chlorate, see Vol. I., p. 618, and for the examination of the various ingredients, nitre, charcoal, and sulphur, see pp. 1, 7, 8. The same points must be noted in judging these substances as in match mixtures.

The determination of aluminium in flares or dust may be carried out by the method of Faber and Stoddard by estimating the reducing power on litharge. The accuracy depends on the formation of a liquid slag from which the globules of lead can easily separate and on the temperature at which the assay is carried out. Three g. of aluminium is mixed with 100 g. of litharge and 30 g. of borax glass and a cover of 25 g. of borax glass added. The fusion takes 20 minutes in a gas muffle.

E. ILLUMINATION AND COLOURED FIRE MIXTURES

In addition to the substances already mentioned, these almost invariably contain potassium chlorate, together with substances, such as strontium, for producing the colours. Strontium salts give a red colour, barium salts a green colour, copper salts blue, and sodium

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salts (e.g. oxalate and carbonate) a yellow colour. For extra brightness, magnesium powder is added. They are accordingly mixtures of combustible substances with compounds which give coloured flames, and like exploding gun-powder, they throw off small particles which continue to burn while in motion, and owe their power of projection

to the combustion. At first sight, it would appear easy to make one of these mixtures, but several factors have to be taken into account, such as the velocity of combustion, which in the case of "stars" should be great, for coloured lights slower, and for flames slowest of all; the temperature at which the substance imparting colour will act best; the formation of slags, and their fusibility. To find out whether these substances are suitable for colour mixtures, they should be thrown in the form of a dry and very fine powder into flames of varying temperatures such as hydrogen flames, the temperature of which has either been raised by oxygen, or lowered with nitrogen, so as to find out the effect of different temperatures. But this test is not always successful; for instance, lithium salts impart an intense carmine coloration to flame, but do not produce a colour of anything like the same intensity in mixtures. The manufacturer mostly tests this by making a small sample mixture, consisting of:—

Potassium chlorate	20 parts
Sulphur	5 "
Gum mastic	1 part

If the substance to be tested gives a good fire coloration with this mixture, it can probably be used.

The following formulæ have been found upon actual trial to yield satisfactory green and red colour mixtures respectively (E. G. Clayton):—

	Green.	Red.
Barium nitrate	60	...
Strontium nitrate	...	63
Potassium chlorate	15	18
Sulphur	13	13
Realgar	11	...
Shellac	...	5
Charcoal	1	1
	<u>100</u>	<u>100</u>

Another green mixture is: barium chloride, 69 parts; lactose, 30 parts; shellac, 1 part. For a yellow light, a mixture of sodium nitrate, 20 parts; sulphur, 20 parts; antimony sulphide, 8 parts; and carbon, 2 parts, may be used. A mixture of powdered pitch, glue, and borax will give an intense yellow flame.

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By mixing together combustible compositions, which give different colours, a tint is obtained, which is nearer to a white than to a mixture of the two colours. On mixing red and yellow a pale orange results; blue and yellow give a not very intense pale green; blue and red give violet, and this is the only good colour obtained by mixing; red and green give white.

For spark compositions the following can be used: nitre, sulphur, meal gun-powder, charcoal, steel and other metal borings, aluminium, magnesium and various alloys, orpiment and antimony sulphide.

A number of phosphorescent light mixtures have been described by L. Vanino. The constituents are heated together for 1 hour, the number of parts being in parentheses:—*Violet-blue*: quicklime (15.0), strontium hydroxide (5.0), sulphur (8.0), magnesia (1.0), sodium carbonate (3.0), lithium sulphate (1.0), and 6 c.c. of 0.3 per cent. aqueous colloidal bismuth solution; or, alternatively, quicklime (17.0), strontium hydroxide (5.0), sulphur (8.0), lithium fluoride (1.0), magnesia (1.0), 1.0 c.c. of 1 per cent. rubidium nitrate solution, and 6 c.c. of 0.3 per cent. colloidal bismuth solution. *Violet*: quicklime (20.0), barium hydroxide (10.0), sulphur (9.0), sodium sulphate (1.0), potassium sulphate (1.0), lithium sulphate (1.5), 2 c.c. of 0.5 per cent. alcoholic bismuth nitrate solution, 1 c.c. of 0.5 per cent. aqueous thallium sulphate solution, and 0.5 c.c. of 0.5 per cent. aqueous thorium sulphate solution (the nitrates may be substituted for thallium and thorium sulphates). *Blue*: strontium hydroxide (15.0), quicklime (5.0), sulphur (8.0), magnesia (1.0), sodium carbonate (3.0), lithium sulphate (1.0), and 6 c.c. of 0.3 per cent. colloidal bismuth solution. *Green*: strontium hydroxide (20.0), sulphur (8.0), magnesia (1.0), sodium carbonate (3.0), lithium sulphate (1.0), and 6 c.c. of 0.3 per cent. colloidal bismuth solution.

Among non-chlorate colour compositions, in addition to these already mentioned, are some containing borax.

Smokeless flash powders have also been described containing up to 28 per cent. of zirconium, zirconium hydroxide and magnesium, barium nitrate, barium oxide and rice starch.

The presence of sodium compounds in certain flame pyrotechnics is to be avoided on account of the masking influence of the sodium flame and also on account of the hygroscopic nature of sodium nitrate which might interfere with the proper functioning of the pyrotechnic. The sodium nitrate can be estimated by the method of Ball. When a mixture of potassium nitrate, bismuth nitrate and caesium nitrate in nitric acid is added to a dilute solution of sodium nitrate, even in presence of large amounts of potassium salts, the sodium is precipitated

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quantitatively in a crystalline form as caesium sodium bismuth nitrite ($5\text{Bi}(\text{NO}_2)_3 \cdot 9\text{CsNO}_3 \cdot 6\text{NaNO}_3$). An improved technique has been described by Faber and Stoddard.

F. POTASSIUM CHLORATE AND SULPHUR

This consists of a mixture, used for adding to illumination mixtures, of 125 parts of potassium chlorate and 35 parts of sulphur. The use of chlorates is restricted in mixtures on account of their sensitiveness and has been made illegal in some countries.

G. "COLD" AND "WARM" MIXTURES

If the components are simply mixed together, the mixtures are known as "cold" mixtures. "Warm" mixtures are those made by fusing the substances together. The following is a "warm" mixture:—Grey mixture, 85 parts; meal powder, 29 parts; and antimony sulphide, 5 parts. This is used for fire balls and for white fire. Bengal lights are also often made by fusion.

H. IGNITION MIXTURES

These are for the purpose of firing inflammable objects at a distance. They must be made in such a manner as to combine the property of burning slowly with the development of as high a temperature as possible. The mixture used in Prussia for this purpose consisted of 76 parts of grey mixture and 24 parts of colophony. In Bavaria a combination of meal powder with "warm" mixture was customary.

I. MIXTURES FOR SPECIAL FIREWORKS

The following mixtures are used. For fuses, a mixture of meal powder, charcoal, and mica; for "golden rain," meal powder, charcoal, and iron filings; for "silver rain," lead nitrate, potassium nitrate, and charcoal; for "comets" a little meal powder and charcoal. Picric acid mixtures were introduced by Dessignolle and Castelaz, by Brugère, and by E. Jacobsen, for causing detonations with coloured fires. With copper powder, green sparks are obtained; with magnesium, white; and with zinc, bluish-white.

The first named used ammonium picrate together with barium nitrate, strontium nitrate, etc.; the last used the picrates of strontium and barium, which, however, have to be fired by means of a fuse. These mixtures are best made by the manufacturer himself from picric

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acid and the respective carbonates. For the testing of picric acid, see p. 44.

A mixture of calcium nitrate and carbonate, potassium nitrate, magnesium or aluminium red lead and calcium resinate may be used as a tracer mixture.

Whistling squibs are made with magnesium picrate. The mixture is prepared according to the formula of the inventor, Weiffenbach, of Stuttgart. Two hundred grams of picric acid and 800 g. of nitre are dissolved in hot water, and saturated with 30 g. of magnesium carbonate, and the precipitated crystals then dried.

Hexamethylenetetramine may be substituted for charcoal, shellac, dextrin, or sugar in pyrotechnics, especially in fireworks for indoor display. Charred woodmeal or sawdust may also be used.

A typical smoke composition is as follows: tetrachlorethane or chloronaphthalene, 40 to 50 per cent.; zinc filings, 35 per cent.; nitre saltpetre, pitch and calcium silicate, 15 per cent.

As an example of a detonating firework composition the following may be given; phosphorus sulphide is mixed with an oxidant and an inorganic binder consisting of magnesium oxide and an alum.

J. MERCURY FULMINATE (see p. 59)

This is used for percussion caps, either alone, or mixed with other combustibles substances, or with gun-powder, potassium chlorate, nitre and sulphur, etc. These additions serve the purpose of retarding the decomposition, and of increasing the volume of the gases formed. Percussion caps are made of thin rolled copper sheet. The following is a prescription for this mixture:—One hundred parts of mercury fulminate are rubbed into a paste with 30 parts of water on marble slabs with boxwood rubbers; to this are added 50 parts of nitre, or 62.5 parts of nitre and 29 parts of sulphur. The paste is dried on sheets of paper, and granulated by means of hair sieves. Some makers, after placing the grain in the percussion cap, cover it with a small copper plate, while others coat the grain with mastic varnish. Discs of varnished tinfoil, or paper, or of both together, are sometimes used. One kilogram of mercury after conversion into the fulminate is sufficient for 40,000 percussion caps.

Analysis of Mixtures containing Mercury Fulminate. F. W. Jones and F. A. Wilcox advise, in a mixture containing potassium chlorate, the fulminate, and antimony sulphide, first to extract the fulminate

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of mercury from a weighed quantity by means of a solution of ammonia in acetone, then the chlorate with water, and to weigh the residual antimony sulphide.

Chlorates are usually determined by conversion to chlorides by a suitable reducing agent and estimation as silver chloride; or by heating with excess of conc. hydrochloric acid, when the gases evolved set free an amount of iodine (estimate with thiosulphate) from potassium iodide equivalent to the weight of chlorine present in the gases evolved. For the presence of potassium perchlorate in ammonium nitrate and chlorate mixtures the method of Bunge may be employed: 100 c.c. of an aqueous extract of the explosive is mixed with 20 to 25 g. of powdered quartz, the mixture is evaporated to dryness and ignited. Potassium is then determined in an aqueous extract of the ash by the perchlorate method, a correction being made for any potassium chloride or nitrate originally present in the explosive. For rapidly determining perchlorate alone in explosives containing only small amounts of other potassium salts and nitroglycerin, 5 g. of the explosive is mixed with 20 g. of powdered quartz, and the mixture is heated in a quartz crucible. The ammonium salts are thus decomposed, and the aqueous extract of the ash is analysed as before.

H. Brownsdon estimates the mercury fulminate by decomposing it with excess of sodium thiosulphate, and determining the resulting alkalinity by $N/10$ sulphuric acid, previously standardised against pure fulminate.

The method has been improved by Philip. He dissolves the fulminate in a large excess of potassium iodide and a known volume of a standard solution of sodium thiosulphate is also added. The excess of thiosulphate is titrated with standard iodine solution after neutralisation with standard acid.

Marqueyrol⁴ extracts the mixture containing mercuric fulminate and other compounds with a 5 per cent. solution of potassium cyanide. The extracted mercury salt is electrolysed and the mercury estimated in the usual way.

The explosive properties of fulminate of mercury have been studied by Berthelot and Vieille, who give the following equation for its decomposition:— $(\text{CNO})_2\text{Hg} = \text{Hg} + 2\text{CO} + 2\text{N}$. When mixed with 30 per cent. of water, it can be rubbed on a marble slab, with a

wooden rubber, or a soft, clean cork, without any danger.

The following are the results, in round numbers, of a series of analyses of several kinds of percussion caps, in one of which lead

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thiocyanate had been used instead of mercury fulminate (E. G. Clayton):—

	1.	2.	3.	4.	5.
Mercury fulminate	33	21	25	27	...
Lead thiocyanate	38
Antimony sulphide	15	45	34
Sulphur	7	...
Ground glass	18	43	...
Potassium chlorate	52	34	23	23	84
	100	100	100	100	100

Approximate weight of charge
per cap G. G. G. G.
0.025 0.046 ... 0.022 0.025

In these analyses, Brownson's method was employed for the determination of the fulminate, the antimony was estimated volumetrically, the lead gravimetrically, and the thiocyanic acid by a colorimetric method; the figures for potassium chlorate were obtained by difference.

II. DETONATORS

Initiating explosives (detonators, including railway detonators) may be examined by the Esop test. In this test, the detonator is mixed with varying amounts of an inert substance (*e.g.* talcum) until a number of cartridges of a mixture do not detonate regularly when fired with the detonator under examination. The two ingredients used in the test are picric acid and olive oil. The strength of the detonator may also be measured quantitatively by the Wohler test. The initiating effect on 2 g. of trotyl (trinitrotoluene) or troxyl (trinitroxylene) mixed with paraffin is measured. Equal weights of the explosive (*i.e.* trinitrotoluene) are mixed with a standard paraffin oil to give a series of samples with varying paraffin-oil content. The explosion is carried out with 2 g. of each grade of trotyl in a copper tube of 10 mm. diameter placed on a plate 5 mm. thick. The maximum percentage of paraffin oil which still allows complete detonation is taken as a measure of the strength of the detonator.

III. PRIMINGS

A. THE FIRING-EXCITER

This consists of a mixture of meal powder and alcohol. A fast exciter consists of 1000 g. of meal powder and 570 c.c. of alcohol; a

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slow exciter of 1000 g. of meal powder and 720 c.c. of alcohol. These mixtures are best made with the hands in a copper pot, or in a porcelain basin. The exciter is painted on to the quick match at the firing hole, where the paper of the covering of the firework has been twisted together, for instance where the fuse is fastened to crackers and squibs. In general all those places which are intended to catch fire are painted with this mixture. If it is intended to stick tightly, a solution of 16 g. of gum arabic in 140 c.c. of water is added. The tests used are similar to those employed for gun-powder (p. 29).

B. SLOW AND QUICK MATCHES, FUSES

Triple and quadruple cotton threads, purified from grease as for gun-cotton, are soaked in quick firing-exciter, and sprinkled with meal powder. After the impregnation they are allowed to lie for six to eight hours, then rolled on a bobbin and passed through a board, provided with holes of various sizes, so as to impart the required strength and uniform thickness to the threads after air drying. They are again passed through the firing-exciter, which has been thickened with gum arabic, then again through the holes in the board, sprinkled

with meal powder and dried; finally they are wrapped in paper, placed in dry boxes, and stored in a dry place. According to the formula used for the Prussian artillery, the following quantities are necessary for a fuse 100 metres long, and 0.52 cm. in diameter:—2.94 kg. of meal powder, 4.35 litres of alcohol, 21.2 g. of gum arabic, and 0.24 kg. of cotton thread. Thus prepared, the speed of burning is 1 metre in 24 secs.

Better fuses are obtained by a previous treatment of the cotton with a special mordant (*cf. infra*).

In the case of a *train of powder* (or *leader*) the fuse is covered. These covered fuses protect the firework against pre-ignition, and also cause a quicker firing. For this purpose the fuses are covered with paper tubes.

Quick Matches or *Paper Fuses* are made of cotton wick boiled in a solution of gum and meal powder and partly dried. The wick is then dusted with meal powder. It may be used in this form or enclosed in a tube, when it burns more rapidly (approximate rate: 1 foot in 1 to 3 secs.). As a rule, they are about 28 cm. long, and 0.33 to 0.21 cm. in diameter.

The Mordant for Fuses serves in the first place to make the fuse more inflammable, and secondly, to ensure a steady and quiet combustion, for instance, as in time fuses. The mordant consists of a solution of 1 part of nitre in 10 parts of water. The dry cotton threads are allowed to remain in this solution for twelve hours, and are then wrung out and dried.

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Slow Matches as prepared for pocket match boxes, are obtained by boiling loosely spun cotton in a solution of lead nitrate, consisting of 1 part of lead nitrate in 10 parts of water or in potassium nitrate; they are then allowed to dry in the air without being wrung out. Another method consists in boiling the cotton in a solution of lead acetate (1 part of lead acetate in 20 parts of water) and when dry, placing them in a solution of 1 part of potassium bichromate in 10 parts of water. The threads so made are yellow, owing to the formation of lead chromate. This fuse smoulders at the rate of about 1 foot in 3 hours, and used when a long delay is required.

In the *Sheune* fuse lead tubing is filled with powdered trinitrotoluene. The explosive is melted and drawn into the tube by suction, and when cold the tube is drawn out to a diameter of 4 mm. The tube may also be filled with molten trinitrotoluene and allowed to cool. The length is increased by hammering. The temperature of the explosive is kept below its melting point during the treatment and a current of air directed on the tube. In this way a more sensitive *cordeau* or fuse is obtained.

Electric fuses are also used.

Fuse Paper. In dry weather this can be used in place of the ordinary fuses, and finds general use for certain firings. It is made by spreading firing-exciter on to both sides of sheets of blotting paper, sprinkling it with meal powder and drying it.

C. GUN-COTTON FUSES

The preparation of gun-cotton fuses is exactly the same as that of gun-cotton. They can be tested as described in the section on Nitrocellulose (p. 32). These fuses transmit fire faster than any other form, and are mostly used for firing large set-pieces; they burn very fast, and will fire a fuse-paper wrapped round them with absolute certainty; they have the further advantage that they can be used in wet weather.

D. PORT-FIRES

These are fireworks which will cause the firing of charges and of other fireworks quickly and safely in cases where the fuse cannot be used. Port-fires must therefore be capable of burning very well, and must not be put out by even the strongest shower of rain. The mixtures employed must be very rich in oxygen, and it is recommended to fuse together the nitre and sulphur mixture used in their manufacture.

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Port-fires are about 40 to 50 cm. long, and should give a flame 8 mm. long. The necessary casing is made of strong cardboard, and is soaked in a solution of nitre so that it should burn easily; the diameter is about 1 cm. The mixture is filled into these cases, about 5 cm. deep at a time, and slightly compressed: sometimes it is moistened with linseed oil. The composition of some typical port-fires is as follows:—

	Swedish Mixture.	French Mixture.	Prussian Mixture.
Nitre	24 parts	6 parts	100 parts
Sulphur	14 "	3 "	100 "
Meal powder	11 "	1 part	85 "
Colophony	1 part	...	7 "

E. COMPOSITION FUSES

These are really only port-fires on a smaller scale; they are fastened to fireworks and effect a certainty of firing. They are made of strong paper, have a diameter of 0.5 cm. and a length of from 6 to 8 cm. They are filled up to 2 to 3 cm. with meal powder, on the top of which a layer of priming-mixture is placed. Such mixtures consist of:—Nitre and sulphur, 100 parts; meal powder, 25 parts. The mixtures used for time fuses can also be employed.

F. TIME FUSES

Many fireworks (set pieces) can only be successful and produce the desired effect if some parts, such as torches, squibs, etc., have a definite time for burning. Time fuses are used for exploding charges, or for igniting fireworks in a definite period of time. These time fuses are tubes filled with a mixture in such a manner that a certain length will burn in a definite time.

As in the case of igniters, the differences in the action of time fuses are based solely on the proportions of a few constituents (powder, nitre, sulphur, etc.), and upon the density of the mixtures. Their examination is conducted as described above. The main requirement in the case of these fuses is to determine the time of burning.

IV. THE DURATION OF BURNING

In fireworks, the maintenance of a definite duration of burning is especially necessary where set pieces are used, or where rotations are required and the like. It is less necessary in the case of rockets, when they are to be let off together in the form of a fan, etc., or in a quantity of squibs, because the composition and compression of the

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mixtures used are sufficient to regulate the combustion. The duration of burning of a mixture is dependent upon:—

1. The composition.

2. The degree of dryness.
3. The degree of fineness, and the thoroughness of mixing.
4. The degree of compression.
5. The area of its burning surface.
6. The area of the delivery opening.
7. The nature of the covering.

From this it is obvious that successful results can only be obtained by working with uniformly made mixtures, with the same covering material, and uniform charging. Small divergences nevertheless occur, but these can be neglected, as they make no difference, when the firework is ignited. Moisture in the mixture retards the firing, not only directly by its presence, but also because it causes reaction, mainly between the sulphur and the metals in the mixture, when the fireworks are stored. The area of the delivery opening retards the firing when it is less than $\frac{1}{4}$ to $\frac{1}{2}$ of the area of the case.

The duration of burning is determined with a stop-watch, and is of importance in the case of set pieces, in which several kinds of mixtures are present. The time can then be regulated by altering the depth of the mixture in the cases; shorter cases for slower mixtures, and longer cases for quicker mixtures, can be used.

V. TESTING FIREWORK MIXTURES FOR LIABILITY TO SPONTANEOUS COMBUSTION

Some compositions used in the manufacture of fireworks have pyrophoric properties; for example, mixtures containing iron filings and sulphur, which have become damp; also certain Bengal light mixtures. Illumination mixtures containing nitrate of strontium or barium, sulphur and potassium chlorate, will often fire of their own accord, after standing for a few hours. This occurs chiefly when the ingredients have been quickly dried before use, and when the mixture is left lying in a warm, moist place. An ignition of this nature can be prevented by making the mixture of pure materials. A better preventive, according to Clarke, is an addition of a small quantity of antimony sulphide, or of a small quantity of sodium carbonate or chalk, as in the case of nitrocelluloses. The latter take up any acid impurities of the sulphur or other components, and form compounds which are inactive with chlorates and nitrates. This treatment is of some use, but the action of antimony sulphide is questionable. Mixtures

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which have become damp, must be dried separately and with great care, as they ignite easily. Mixtures containing copper oxide also fire readily, but this can be prevented by substituting copper carbonate for the oxide. Traces of permanganate or bromate are also dangerous.

The test proposed by Meischmeier is carried out as follows:—Five grams of the mixture is slowly heated in a dish on a sand-bath, to 100°, and kept at this temperature for two hours. If it is now moistened with water, and again dried, it should not ignite spontaneously.

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