

THE INSTITUTE OF PETROLEUM.

A meeting of the Institute of Petroleum was held at Manson House, 26, Portland Place, London, W.1, on Wednesday, June 11, 1947, when the chair was taken by Mr J. S. Jackson, Vice-President.

MR J. S. JACKSON : It is my pleasing duty to introduce Dr G. L. Riddell, who is the Director of the Printing and Allied Trades Research Association. He is a recognized authority on printing inks, printing, and all matters connected therewith, and we are very honoured to have him here to-night to serve as technical Chairman, to preside during the presentation of the paper, and to conduct the subsequent discussion. I offer him a very special welcome, and I invite him to occupy the chair.

DR G. L. RIDDELL, having formally occupied the chair, said : I thank you, Mr Jackson, for your kind comments. I am afraid I am not an authority on anything, certainly not on printing inks; they are much too difficult.

We are to have presented to us a joint paper by Dr Healey and Dr Ivanovszky. I do not think I need to introduce Dr Ivanovszky to anyone in this room; he is sufficiently well known to you as a Fellow of the Institute. But I may perhaps be allowed to say a word about Dr Healey. He is well qualified to discourse on this subject, because until the war he was the chief chemist of one of the printing ink companies; one of the companies which utilized in their manufactures a considerable quantity of the products of the petroleum industry.

I am a little disappointed that there are not more printing ink people here, because I should regard this meeting as providing a first rate opportunity for them to tell you face to face some of the things they say behind your backs about some of the products with which you supply them.

DR HEALEY then presented the following paper.

PETROLEUM PRODUCTS IN THE PRINTING INK AND ALLIED INDUSTRIES.

By A. C. HEALEY, Ph.D., M.Sc., F.R.I.C., and L. IVANOVSKY (Fellow).

PRINTING inks consist of a coloured pigment or dye dispersed or dissolved in a suitable medium. The purpose of the medium, otherwise called vehicle, or varnish, is first, to carry the pigment during the printing process from the ink duct or reservoir, via the printing plate, to the paper, and secondly, to fix the pigment to the paper after printing.

Petroleum products are of very considerable importance in printing ink manufacture, both as colouring materials in the form of carbon black and lamp-black, and as components of the vehicle. Before discussing the uses

of petroleum products in printing ink manufacture, it is necessary to consider the mechanism by which a fluid ink is converted into a rub-proof film in the dried print. The most important methods by which this change occurs are :—

1. Oxidation or polymerization, whereby a drying oil such as linseed oil is converted from a liquid to a solid state ;
2. Absorption of the ink into the paper ;
3. Evaporation, whereby a volatile solvent evaporates, leaving a solid residue behind ;
4. Gelation.

Other methods of minor importance exist, but are usually only employed in special cases. Here are two examples :—

Freezing, whereby an ink is used which is solid at normal temperatures. The printing-press is heated sufficiently to melt the ink during the printing process. The ink resolidifies immediately it touches the cold paper.

Precipitation, whereby the solid portion of the ink is precipitated after printing by spraying the freshly printed paper with a non-solvent of the resinous constituents of the vehicle.

It does not follow that a particular ink dries by one process only. In fact the reverse is usually the case and the drying is due to a combination of these processes.

There are three main methods of printing :—

1. Typographic (letterpress), in which the ink is applied by suitable rollers to the raised portions of the surface of type or blocks and from them transferred to the paper ;
2. Lithography, in which the printing plate is a flat surface of either stone, zinc, or aluminium, a portion of which is rendered greasy and so receptive to ink, the remainder of the plate being made ink-repellant ;
3. Intaglio printing, which employs a plate having the design etched or engraved below the surface of the plate. The whole plate is covered with ink and is then wiped clean, leaving ink only in the etched areas, from which it is subsequently transferred to the paper. Photogravure is the best-known type of the intaglio printing processes. Less important are die-press, copper, and steel-plate printing.

The three printing methods are illustrated in Fig. 1, which shows a representative section of the printing surface for each process. It will be seen that the inked sections shown in black in the diagram are above the level of the non-printing portions in typographic printing, on this level in lithographic processes, and below it in intaglio plates.

The types of letterpress printing machines are shown in Fig. 2 : (a) Platen presses, in which the printing forme is flat and the paper pressed against it all at once ; (b) Cylinder presses, in which a flat printing plate is also employed, whilst the paper is pulled round the surface of a cylinder in such a way that it progressively makes contact with the forme, which is moving below the cylinder at the periphery speed of the latter ; (c) the rotary press,

in which continuous roll or web of paper is used, which passes round a cylinder known as the impression cylinder. A curved printing plate is employed, which is pressed against the paper as it passes over the impression cylinder. Rotary presses are used for high-speed printing, for instance, in the production of newspapers. Some rotary printing-presses will print, cut, and fold ready for despatch as many as 50,000 newspapers per hour. Platen and cylinder presses are much slower and print up to about 5000 sheets per hour.

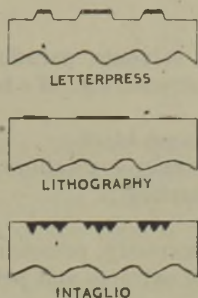


FIG. 1.
PRINTING METHODS.

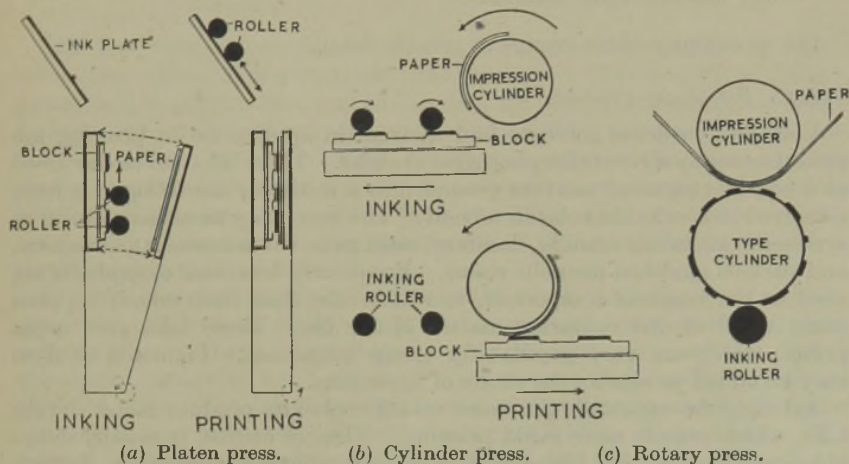


FIG. 2.
TYPES OF PRINTING MACHINES.

Typographic and lithographic inks usually dry by absorption, oxidation, or polymerization, while intaglio inks usually dry mainly by evaporation assisted by absorption.

Letterpress and lithographic inks are composed of a suitable pigment mixture dispersed in a vehicle consisting of drying or non-drying oils, to which some resin may have been added. When drying oils are used, it is generally necessary to incorporate driers.

In photogravure inks the pigment mixture is dispersed in a vehicle consisting of a resin dissolved in a volatile solvent.

TYPES OF PETROLEUM PRODUCTS USED IN PRINTING INKS.

Petroleum products are used in the printing ink and allied trades in three different ways—namely, as components of printing inks, as cleaning agents, and as lubricants for printing machinery. A wide range is used, which may be classified as follows :—

- (a) Volatile petroleum solvents, paraffin, and close-cut fractions of high-boiling petroleum solvents, *e.g.*, of a boiling range of 260°–290° C;
- (b) Mineral oils;
- (c) Carbon black and lamp-black;
- (d) Paraffin wax and microcrystalline waxes (petrolatum waxes, petroleum ceresines, ozokerites);
- (e) Petroleum jelly;
- (f) Asphalts, or more correctly, petroleum bitumens;
- (g) Petroleum aromatic extracts and petroleum resins;
- (h) Naphthenates;
- (i) Greases;
- (j) Wetting agents;
- (k) Miscellaneous materials.

Let us examine these groups in greater detail.

Volatile Petroleum Products.

Volatile petroleum solvents find their main application in printing ink manufacture as solvents for photogravure inks. These inks can be described as a suitable pigment mixture ground into a medium, consisting of a resin dissolved in a suitable volatile solvent. The resin may be either natural or synthetic, including manilla, dammar, ester gum, coumarones, zinc resinate, and various modified phenolic resins. Frequently bitumens or asphalts are used as the resinous component, in which case their dark colour supplies some or all of the colouring matter of the ink. These inks give sepia prints, which are very popular for cheap magazines. Pigments or dyes may be added to modify the shade of these inks.

As might be expected, the more volatile solvents produce faster drying inks, which permit more rapid printing. This, of course, is usually desirable, particularly for high-speed magazine printing. However, factory regulations in some areas may prohibit the use of inks having a flash-point under 73° F. It is usually advisable to employ a solvent having a narrow boiling range and a minimum of tailings of slower drying constituents. These are liable to remain for some time in the freshly printed sheets and cause the ink film to remain "tacky" for an unnecessarily long time after printing. This may be sufficient to cause the sheets to stick together in the pile at the delivery end of the printing press.

It is, of course, essential that the solvent used in a photogravure ink should be a satisfactory solvent for the resin. Owing to the generally improved solubility of resins in aromatic solvents, it is usually considered

advantageous if the aromatic content of the petroleum solvents employed is as high as possible. In fact it is quite common to use entirely aromatic solvents such as benzene, toluene, or xylene.

The following table, containing data from the "Science of Petroleum," gives the properties of some petroleum solvents used in photogravure inks :—

Sp. gr. at 60° F	0.768	0.792	0.80
Distillation :			
Initial boiling-point, ° C	75	100	115
50% distilling to, ° C	80	108	129
Final boiling-point, ° C	95	120	160
Flash-point, ° F	below 73	below 73	45 app.
Aromatics, % by weight	25	43	40
Kauri-butanol number	49	56	53

The kauri-butanol test is a dilution test, which consists essentially in titrating a given volume of a kauri solution in butanol with the solvent under examination, the end-point being reached when the opalescence caused by the precipitation of the resin is sufficient to cause blurring of normal print.

A typical basic-formula for photogravure inks would be :—

	Per cent
Pigment	20
Resin	20
Solvent	60

The less volatile petroleum solvents have some application in letter-press inks. Paraffin is sometimes added to reduce the viscosity of the ink, to increase its penetration, and to decrease the tack, particularly in inks for fast running rotary and cylinder presses. Paraffin is a frequent component of the so-called "quickset" inks. These inks do not dry on the printing-press, but nevertheless dry very quickly after they are transferred from the block to the paper. This effect is produced by the penetration of one component of the ink into the paper, causing the remainder to gel and to produce rapid drying of the ink.

A recent development in high-speed printing is the "Vaporin" process. A special ink is used which consists of a pigment, or pigment mixture, dispersed in a vehicle consisting of a resin dissolved in a solvent that is essentially non-volatile at ordinary temperatures, but easily volatile at elevated ones. The ink is printed in the conventional manner, but after printing the paper is passed at high speed over a series of gas flames. The solvent is evaporated and the vapours ignited, but the paper is moving so rapidly that it is not scorched. The removal of the solvent in this manner produces almost instantaneous drying of the print. This method of drying prints is advantageous in high-speed magazine printing. The solvents first used were synthetics having a boiling-point between 200° C and 250° C, such as butyl carbitol acetate. High boiling petroleum solvents with a narrow boiling range have subsequently been used; they have the advantage of being considerably cheaper in price. The solvents used for this process should have no objectionable odour and be free from "heavy ends."

A proportion of petroleum solvents is usually included in silk screen inks. These inks are printed by a stencil process using a silk screen, portions of

which have been filled in, leaving the design open. The filling-in may be done in various ways, such as pasting paper over the screen or by photographic means, using dichromated gelatine. The ink is applied to the paper through the screen by means of a roller or squeegee.

Die-press inks, too, usually contain petroleum solvents. These inks consist of a pigment mixture dispersed in a resin solution. They are, however, considerably stiffer than photogravure inks. Die-press printing is an intaglio process, used to produce embossed printing, such as that commonly used for letter headings.

Petroleum solvents are frequently also used for cleaning purposes. It is necessary at times to remove ink from the rollers of the printing-press and from the printing forme. This is usually done at the end of a shift or when changing from one colour to another.

The cleaning process is an important one, but is unfortunately "messy" and expensive in that it is unproductive. Various surfaces have to be cleaned, including metals, glue-glycerine composition, rubber, either natural or synthetic, and possibly stone. Some care has to be taken to choose the most suitable solvent for each particular purpose. Kerosine is probably the most common material used for cleaning purposes and is generally satisfactory for cleaning metal and glue-glycerine composition rollers. It may leave an oily residue on drying, which is sometimes advantageous, but may be detrimental on other occasions. However, kerosine should not be used on rubber rollers, blocks, or blankets.

For cleaning the forme during proofing, it is advantageous to use a fast-drying solvent, such as aviation spirit, as it dries very quickly from the block and does not leave any oily residue which might prevent a good proof from being pulled. Commercial petrol and its mixtures with kerosine may be used for cleaning the block while it is on the machine.

Cleaners for rubber surfaces should be readily volatile and not leave any oily residue, which would cause rapid deterioration of the rubber. With some types of oil-resistant synthetic rubbers this is not so important.

The boiling-point of solvents is insufficient to give a true idea of their evaporation properties. It should be realized that higher boiling solvents may evaporate faster than others with lower boiling-points. The evaporation ratio depends on the vapour pressure, the viscosity, and the spreading capacity of the respective solvents. The surface from which evaporation occurs obviously has some bearing. Absorption, or should we say adsorption phenomena, between solvent and surface also are of some importance. The fact that the rate of evaporation is considerably and variably influenced by the dissolved substances is well known, but often forgotten.

Mineral Oils.

Mineral oils are used very extensively in the manufacture of news inks and magazine inks. They do not dry to a hard film in the same way that linseed oil does. Consequently, inks based on mineral oils must dry by penetration into the paper rather than by oxidation. For this reason they are always printed on fairly absorbent paper. These inks are almost always low in price and are used on cheap paper. Mineral oils are cheap compared with the vegetable drying oils, and are very well suited to the manufacture of cheap inks.

In the United States of America about 100,000 tons of news ink, valued at nearly \$9,000,000, are used annually. They will probably contain over 80 per cent petroleum oils and about 10 per cent of carbon black derived from petroleum gases. These figures obviously do not include the considerable amount of mineral oils used in other types of printing ink.

Products derived from paraffin-base crudes were first used for the production of news inks, but have now generally been replaced by oils that are predominantly naphthenic, as these usually give inks of better characteristics. Oils that are essentially naphthenic in character have good pigment-wetting properties and produce inks that have good flow. Oils that only badly wet the pigment tend to produce inks having a poor flow.

According to J. J. Matiello ("Raw Materials Used in Printing Inks," p. 82), the naphthenic oils, besides giving inks possessing good working characteristics, also impart to the ink a remarkably lasting plasticising effect. This does not mean that the inked surface is either tacky or greasy, but that it is pliable and not easily cracked during normal usage, in addition to its being dry and non-tacky.

It is more difficult, in general, when using a high paraffinic type of oil, to obtain a printed surface free from offsetting. Offsetting takes place when the fresh print transfers some ink to the back of the next print in the pile at the delivery end of the press.

It is desirable that the oils used should possess as little colour as possible, otherwise a noticeable halo may make an appearance or a coloured stain may occur on the reverse of the paper, due to the vehicle "striking through" the paper. Low grade unrefined oils probably contain coloured material that may be deleterious. It is considered good practice to use clear, distilled oils in the manufacture of inks.

There are, however, other characteristics to be considered. Mineral oils used in printing ink should possess the ability of easily wetting the pigment, as oils of poor wettability produce, as already mentioned, inks that possess a buttery consistency. These "short" inks do not print satisfactorily and "lengthening" agents have to be added.

Better dispersion may result in the manufacture of news inks, using darker oils which contain a small proportion of materials that act as wetting or dispersing agents. On the other hand, these oils are likely to produce more staining on the back of the sheet. It may be necessary in practice to strike a balance by a judicious mixture.

Mineral oils, particularly those of high naphthenicity, may be used in conjunction with litho varnishes, when printing on certain types of paper. Inks made in this way dry by a combination of oxidation and absorption. A somewhat greater proportion of driers is usually incorporated into such inks, than into inks that are made entirely on a drying oil basis.

The viscosity of the mineral oils used in printing inks varies considerably. For example, a pale oil of Redwood viscosity of 70 and a dark oil having a viscosity of 250 Redwood, both at 140° F, are used for news inks.

The heavy machine oils are the most important. They possess good working properties and impart rapid setting to the ink. The lighter machine oils are sometimes used to replace part of the linseed oil in inks for fast running rotary and cylinder presses. The viscosity of an oil may,

of course, be adjusted by the addition of bitumens, resins, low viscosity oils, solvents, etc.

The following is a typical formula for news inks :—

	Per cent.
Carbon black	13
Dye toner (oil-soluble methyl violet or indulene)	0.3
Oleic acid	0.7
Mineral oil	76
Gilsonite or rosin varnish	10

Typewriter ribbon inks and duplicating inks both may contain mineral oils.

Mineral oils are also used, of course, for the lubrication of printing-presses and printing-ink mills.

Lubricating oils are normally preferred for lubricating printing-presses, although also greases are sometimes used. Clearance in printing machinery construction must be very small, many of the moving parts being delicate, and the room temperature is usually rather high. These reasons necessitate the use of very stable lubricants, and consequently non-compounded mineral oils are used. Specially refined oils are needed for the huge high-speed rotary presses. The flash-point of these oils should preferably be over 150° C and the congealing point below — 5° C. The viscosity of the oils used for the small slow-moving presses should be 180–220 Redwood I at 50° C, whilst for the larger slow-moving machines more viscous oils up to about 300 Redwood I are often chosen. For the lubrication of fast-running large rotary presses, generally thin oils are used with about 120–150 Redwood I, but oils of other viscosities are also employed. The acid value should be maximum 0.4 for distillates and 0.1 for refined oils. Ash, water, and asphalt contents of all oils should be practically nil.

For the gear-wheels of typesetting machines a thin refined lubricating oil 70–120 Redwood I at 50° C is recommended. The flash-point should be 170° C minimum, and acid, ash, and asphalt should be absent. For the casting portion of the machine, oils have to be used with a viscosity of minimum 350 Redwood I at 50° C and a flash-point of minimum 240° C. For the lubrication of the keys of the typesetting machines high grade white oil or acid-free bone oil are recommended. The relatively slow-moving linotype machines are usually lubricated with grease. Owing to the high precision of the machine only unloaded greases should be used; sodium soaps are particularly suitable.

Carbon Black and Lamp-black.

Carbon black, prepared by the partial combustion of natural gas and petroleum gases, is by far the most important pigment used in the manufacture of printing inks. Carbon black is the ideal pigment for printing inks, as it possesses practically every desirable characteristic. It is absolutely fast to light, fats, waxes, acids, alkalis, soap, solvents, heat, and all chemical reagents to which prints may be subjected. Moreover, the pigment is satisfactory from the point of view of the printer. Carbon black has good tinctorial strength and is not abrasive; inks made from it print satisfactorily. Most important is the fact that carbon black is inexpensive. Other pigments, being less satisfactory in many respects, often cost ten or twenty times as much as carbon black. Carbon black has only

two minor drawbacks in printing ink manufacture. First, it has a somewhat brownish tone that is considered rather objectionable. This can easily be overcome by the addition of a little blue pigment or dye, such as Prussian blue, induline, or other fat-soluble aniline dyes. Secondly, carbon black possesses the disadvantage of slowly adsorbing the drier content of the ink, with the result that the latter gradually dries more and more slowly. This is overcome by adding a higher proportion of drier than would be used with other pigments.

Although the bulk of the production of carbon black is used in the manufacture of rubber goods, the printing ink industry is the second largest user of carbon black.

In 1945 the United States used 1,052,798,000 lb of carbon black in rubber manufacture and 22,824,000 lb in the printing ink industry. The paint industry, the next largest consumer, used only 7,421,000 lb.

The bulk of the carbon black is manufactured by the channel process in which the gas is burnt in suitable burners and the flame allowed to impinge on a moving iron channel on which the carbon collects. Blacks made by this process yield "short" inks.

For good quality half-tone and lithographic inks, the so-called "long" carbon blacks are used. This type of carbon black is deposited on rotating rollers. They differ from the "short" carbons in possessing a surface structure that enables them to be easily wetted by a slightly acid vehicle such as lithographic varnish. Consequently a higher proportion of the pigment can be included in the ink. Good flow properties are maintained, and the viscosity and yield value of ink is not excessively increased.

Carbon black has almost entirely superseded lamp-black, which has a much lower tinctorial strength, but possesses a more desirable bluish undertone. Lamp-black still finds application in some types of printing ink, particularly in matt inks. It is prepared by the combustion of various carbonaceous materials, including petroleum.

Carbon black has the smallest particle size of any of the commercially available pigments.

Petroleum Waxes.

Waxes are very important additives to printing inks. In general, their addition to letterpress and lithographic inks "shortens" the ink. That is to say, waxes reduce the length to which a thread of the ink can be drawn. The reduction in length of an ink tends to make it less tacky, which lessens the tendency of the ink to "pick" or "pluck" the surface of the paper. This can occur when the paper is pulled away from the inked block if the cohesive forces of the ink are greater than the adhesion of the surface of the paper to the underlying layers. Moreover, the addition of waxes tends to reduce "set-off."

Most waxes, including paraffin wax, find use in the formulation of printing inks. There are some specialized applications of waxes, such as the manufacture of metallic inks. Without the addition of some wax, it is often difficult to obtain either satisfactory adhesion of the metallic powder to the paper or good "leafing" of the metallic particles. However, beeswax or some of the harder vegetable waxes are generally used for this purpose.

Waxes that possess a tendency to crystallize may be added to letterpress inks to produce a matt effect.

Sometimes, the inclusion of wax may improve the adhesion of the ink film to certain surfaces.

Waxes are usually added to inks as a previously prepared composition, normally containing suitable waxes in mixture with oils or solvents. The following is a characteristic formula :—

	Per cent
Thin varnish	36
Beeswax	28
Paraffin wax	24
Cobalt naphthenate	12

A new and novel application of waxes in printing inks is in the so-called "cold-set" inks. These are inks that consist of a pigment or pigment mixture dispersed in a wax. The ink is solid at normal temperatures, but easily liquefies by the application of heat. The ink is printed on a heated press, thus being in a liquid condition during printing, but on contact with the paper, the ink solidifies immediately. This process enables printing to be done at a higher speed than would otherwise be possible with the conventional inks.

Waxes are also used very extensively in the allied industry of carbon paper manufacture, in particular, waxes (or mixtures) containing a higher proportion of free fatty acids. Carbon paper consists of a special, thin, strong, paper which has been coated with a film of a wax-oil composition, suitably coloured with either a pigment or a dye. Usually, mixtures of several waxes are employed.

Letterpress carbon paper inks are a special type of carbon paper ink that is printed from a block so that only a portion of the paper is coated. For example, many commercial forms have to be signed, but only in a special place. The back of the signature space is printed with one of these inks.

At one time molten wax was sprayed over the freshly printed sheet to prevent the ink film from offsetting on to the back of the next sheet. The wax particles formed a series of small hills which prevented actual contact between the ink film and the next sheet. Only a very small amount of wax was used so that the particles were not noticeable. This method is now obsolete, and a spray of gum solution, such as gum arabic, is largely used instead.

Waxes are also essential components of lithographic crayons which are used for writing or drawing on lithographic plates of stone, aluminium, or zinc, to provide a greasy surface that will be receptive to ink during printing.

In addition, waxes form the principal ingredient of ordinary marking crayons, as well as pencils for writing on glass, and the stencil sheets for duplicating machines.

A considerable amount of paper is impregnated with paraffin wax to render it moisture- and vapour-proof.

Waxes are also used in the production of electros. These are duplicates of letterpress printing plates, prepared by making a wax negative replica of the original plate which is subsequently covered with graphite to render the surface electrically conducting. Copper is subsequently deposited on the

graphited wax surface to form a printing surface. In this way a duplicate of the original block is obtained. The wax used for this process should have a fine grain and be tough and resilient.

Waxes are sometimes added to typewriter ribbon inks.

A small proportion of wax may be added to the heat-drying inks of the "Vaporin" type. This will reduce the tendency to offset, should the ink not be completely dry when the prints come from the heaters. It would also increase the time that the ink would remain on the press without drying by forming a protective wax film over the ink, thus reducing any possible loss of solvent at room temperature.

Petroleum Jelly.

Petroleum jelly is frequently added to printing inks to reduce tack and to prevent "picking." When printing on non-absorbent papers, an excess should be avoided, or the drying may be impaired. It is a common constituent of ink modifiers which are sold to the printer to enable him to adjust the properties of inks.

Petroleum jelly is sometimes recommended for carbon paper inks. Of course, this depends on the nature of the waxes forming the basic material.

It may also be added to reduce the speed of drying, particularly in the case of inks that tend to dry on the printing-press itself.

Bitumens.

Bitumens find several applications in printing ink. In photogravure inks they are used as resin component. Their dark colour, however, contributes very considerably to the colour of the ink. Bitumens are, as already mentioned, extensively used for the very popular sepia tone inks in some illustrated magazines. The colour may, of course, be modified or embellished by the addition of pigments or dyes. Bitumens are also used in some cheap black letterpress printing inks used for printing magazines and books.

Bitumens also find some application in producing etching resists in the preparation of printing surfaces. They may be applied either in the form of a solution, or powdered bitumen is sprinkled over a photogravure plate, which is subsequently warmed.

On exposure to light thin asphalt films are rendered less soluble in solvents. This effect is intensified if the asphalt is pretreated with sulphur, a process being used in the preparation of printing plates.

Powdered asphalts may also be dusted on blocks during the etching stage to prevent undercutting.

Petroleum Aromatic Extracts and Resins.

The use of petroleum aromatic extracts in printing inks appears to be increasing. Possessing some drying properties, they can be used as a partial replacement of linseed oil, rosin, or rosin oil, particularly in some of the cheaper types of inks. However, the extracts are mainly used in those inks which dry by penetration.

The extracts, on the other hand, have characteristic properties of their own that make them of value in the manufacture of printing inks. Their main value lies in their extra wetting properties and their dispersing effect

on the pigments in the ink. They reduce "cheesiness" of the ink and impart flow.

A wide range of petroleum aromatic extracts is available, ranging from mobile to viscous liquids and even to solid resins. Generally, the ink-maker favours the relatively low viscosity grades that are easy to handle. The viscous and solid grades, however, are used when it is desired to increase the viscosity of the vehicle. Nevertheless the extracts have not reduced the use of the mineral oils themselves, which, of course, are considerably cheaper than the extracts.

The extracts have also been suggested as a partial replacement of rosin in the sizing of paper ("Technical Bulletin of the Paper Makers' Association," Spring 1943, pp. 1-3).

An excessive use of petroleum aromatic extracts in printing ink formulation may make the ink too treacly and reduce the rate of penetration into the paper, by binding the vehicle too firmly to the carbon after printing, making the prints tacky and slow-drying. The optimum amount of extracts used depends on the particular oil and carbon black used.

It may be advantageous first to grind the pigment in presence of the petroleum aromatic extract, and then to add the remainder of the vehicle.

Naphthenates.

Oil-soluble metal soaps, principally of cobalt, manganese, and lead, are extensively used as driers in printing ink to promote the oxidation and polymerization of the drying oils. In the past, fatty acid soaps, such as linoleates, were mainly used for this purpose. More recently, however, salts of naphthenic acid have been introduced with advantage. Commercial naphthenic acid is chiefly a mixture of monobasic acids containing pentamethylene nuclei. Compared with the linoleates, the naphthenates have a higher metal content and can consequently be used in smaller proportions. They have improved solubility and their solutions do not skin or precipitate on storage.

Other naphthenates, such as zinc naphthenate, have limited application in printing ink. They may be used to facilitate grinding and dispersion of the pigments and to reduce drier absorption in black inks. Aluminium naphthenate finds application in some types of inks to reduce penetration of the ink vehicle into the paper.

Greases.

Greases, that is to say, suspensions of soaps, chiefly sodium or calcium soaps, in mineral oils, are often added to letterpress printing inks to shorten the ink and to remove excessive tack. The addition of greases to lithographic and offset inks is not advisable, owing to their tendency to cause emulsification of the damping solution.

Only small proportions of greases are added, as an excess can reduce the tack of an ink to such an extent that the ink will not turn in the duct and will fail to distribute properly on the press. Moreover, the ink is liable to strike through the paper after printing and to cause a greasy stain on the back of the print. The addition of too much grease may also impair the drying of the ink.

In the first quarter of 1946, 32,000 lb of greases "other than wool fat"

were used in the United States of America in printing ink manufacture (U.S. Department of Commerce).

Wetting Agents.

Water-soluble wetting agents have found only slight application in printing inks, largely because the orthodox printing inks are not water soluble. On rare occasions they may be added to spirit inks. In recent years some attempts have been made to produce water-based photogravure inks. This has been done most extensively on the Continent during the war years as a result of the shortage of petroleum products.

In America some attempts have been made to produce water-based news inks. In both these cases quicker drying may result from the inclusion of wetting agents in the inks, which would increase the ease of absorption of the ink into the paper.

Wetting agents may be added to typewriter ribbon inks of the glycerine type to increase penetration.

Oil-soluble wetting agents do not appear, as yet, to have found much application in printing inks, but they may find use to promote wetting of the pigment and to facilitate grinding. This is probably an interesting field for the application of oil-soluble petroleum sulphonates.

Miscellaneous Products.

A wide range of synthetic products is now derived from petroleum, cracked petroleum, and petroleum gases. The production of these products does not rely entirely on petroleum, as other starting materials are also available. A number of these synthetic products are used in the manufacture of printing inks. In most cases, however, the materials find only a limited application.

Alcohol, which can be prepared from ethylene, is the commonest solvent for spirit inks. They are rapid drying letterpress inks which are printed from a special printing press, usually from rubber blocks. Spirit inks usually consist of an aniline dye dissolved in alcohol; the solution may contain tannic acid to assist in fixing the dye and a resin, usually shellac. Occasionally, pigment dispersions are used in place of dye solutions. Such inks are widely used for printing paper bags, metal foils, cellophane sheetings and for other purposes.

The vinyl resins, *e.g.*, vinyl acetate, which can also be manufactured from ethylene, are sometimes used as film-forming constituents of spirit inks, particularly in the formulation of inks intended for printing on moisture-proofed cellophane, plastic films, and metal foils.

Acetic acid, prepared by the oxidation of ethyl alcohol, is sometimes used in spirit inks to increase the solubility of the dyestuff in the ink.

A number of "nitrocellulose" solvents can be prepared from petroleum products, for instance, acetone, methyl ethyl ketone, diacetone alcohol, isopropyl alcohol. These solvents find limited application in the formulation of special types of photogravure and spirit inks, mainly where inks are required for printing on metal foils or cellophane, particularly if moisture-proofed.

Glycerine, which can be prepared from allyl chloride, which in turn is derived from propylene, is frequently added to spirit inks. Other secondary

solvents for spirit inks are, for example, alcohol and glycol esters. Glycerine usually forms the basis of hectographic inks, recording inks, and stamp-pad inks. Typewriter ribbon inks may consist of dye solutions in glycerine.

Glycerine is an important material in synthetic resin manufacture, particularly of those types which are largely used in printing inks. One of the main uses of glycerine is the reduction of the acidity of certain types of resins, and in particular to "harden" rosin in the manufacture of ester gums. Alkyd resins, which are largely used in tin printing inks, are usually derivatives of glycerol.

A mixture of glue and glycerine forms the flexible composition which is the most frequently used material for making printing rollers. A similar material is used for hectographic masses.

It is not customary to add synthetic solvents to letterpress inks, most of these solvents being much too fast-drying. However, very occasionally some of the slow-drying glycol derivatives, such as butyl carbitol, are used as reducers. Synthetic solvents can also be used in the previously mentioned heat drying inks of the Vaporin type.

Various synthetic "rubbers" are derived from petroleum sources. Some of them have superior oil-resisting properties, which are advantageous for the manufacture of printers' rollers and offset blankets.

A number of synthetic petroleum derivatives are used as intermediates and may be used for pigment manufacture.

Some of the petroleum-derived synthetic solvents, such as diacetone alcohol, may be used to remove ink from printers' rollers. The cost of these solvents usually only warrants their application if the ink, having been allowed to dry on the rolls, cannot be removed with petrol or paraffin.

CONCLUSION.

There is no such thing in the printing ink industry as "standard formulæ." Each manufacturer formulates his products according to his own experience. Consequently different manufacturers may use widely divergent formulæ, using different materials to produce inks of approximately similar characteristics. As a result, we have found it difficult in many cases to specify precisely the qualities that are required in petroleum products to meet any particular demand in the printing ink industry.

DISCUSSION.

THE CHAIRMAN (Dr G. L. Riddell) : I am sure you will agree that we have listened to a most stimulating paper. I always welcome this kind of paper, providing as it does an opportunity for the representatives of two different industries to get together and to discuss their common problems. It is particularly useful to those of us who work in the printing and printing ink industries because, as you have gathered from the paper, the printing industry uses a large number of materials in many different ways. The printing industry uses these products in comparatively small quantities, with the result that it has become something of a Cinderella so far as raw materials are concerned. You who are accustomed to produce enormous quantities of petroleum products for various purposes should realize that

there is a printing ink industry and that it is worthy of some attention. For that reason alone we should be very grateful to the authors for having presented the paper this evening.

For you gentlemen in the petroleum industry the meeting affords an opportunity to gain first-hand information on the properties your materials should have if you are to satisfy that very difficult person, the printer.

MR P. KERR : In the part of the paper dealing with bitumens the authors state that the effect of light on thin asphalt films is intensified if the asphalt is pretreated with sulphur. Does that mean that the asphalt is to be heated with sulphur ?

DR HEALEY : " Pretreatment " means heating with sulphur.

MR G. W. WHITFIELD : The authors mentioned that naphthenic oils have good pigment-wetting properties. Do they not consider that unsaturated and aromatic oils are also satisfactory in this respect ?

DR HEALEY : Yes, I think I would agree with you.

MR WHITFIELD : I would suggest that the position may be summarized as follows : When selecting a mineral oil of a given boiling range and/or a given viscosity, then in general an oil with a higher specific gravity is likely to possess better pigment-wetting properties than one of low specific gravity.

DR HEALEY : Yes, I think that in general I would agree.

MR A. J. GOODFELLOW : Dr Healey has laid considerable stress on the rate of evaporation. Could he enlighten me as to the methods used to determine that factor ?

DR HEALEY : From the practical point of view I think you would take the ink containing the solvent, print it, and note the time of drying.

DR IVANOVSKY : I think the most commonly used method is to place a few drops, say, 0.5 cc, on a piece of filter paper and to note how widely the solvent spreads, how deeply it penetrates, and how quickly and completely the transparent spot disappears. Oil, of course, would show the phenomena of spreading and penetration, but would not dry by evaporation. I think Dr Healey is right, that the drying of the ink is tested simply by the practical test of printing with it.

As to the relation of boiling point to the rate of evaporation, etc, this matter is primarily of importance in connexion with solvents, but has obviously some relevance to the application of oils. Solvents mixed with oils affect spreading and penetration (and thus also drying) of the latter, which are to some extent accelerated. Some years ago, a pamphlet published by the I.G. Farbenindustrie listed the evaporation rates and boiling points of a range of solvents, showing quite clearly that the boiling point is a very poor yardstick for the drying or evaporating properties. How far this knowledge can be linked up with the drying of oil cannot be stated generally, but largely depends on the particular circumstances.

MR H. A. IDLE : As a member of the printing ink family I would like to express our thanks to the petroleum industry for having so many times "saved our lives" during the long period of shortages. However, I look forward very much to the days when we shall not just be told "That is the product, get on with it." It will be very nice when we can get back to the condition in which there will be sufficient products available from which to choose the best for every different purpose.

DR Y. ZAKY : Could Dr Healey say something about the future possibilities of the aromatic extracts in the printing ink industry? Are they likely to part replace linseed oil permanently, or is it that, simply because of the shortage of linseed oil, manufacturers of printing inks have been driven to use them unwillingly? In other words, is the use of extracts in the ink industry likely to discontinue as soon as linseed oil becomes again freely available on the market?

DR HEALEY : That is a question which to some extent depends on the petroleum industry. The suitability of these products for printing inks has been improving; the products we are now obtaining are substantially better than those we obtained before the war, but they are still not entirely what we should want. We cannot use them to replace linseed oil completely, and we cannot use them to replace petroleum oils completely. Moreover, quite a large amount of printing is done with light coloured inks, and most extracts are sufficiently dark in colour to upset the tone of any brightly coloured or pale inks, where it is desired to preserve quality of tone. If we could obtain extracts of improved drying qualities and of light colour, I think their use would increase substantially. I fancy also that many printing ink chemists are conservative and are inclined to use the same materials as were used a long time ago. Nevertheless, I think you will find that the use of the extracts will increase, particularly if we can improve the colour and the drying times. I do not think that an improved supply of linseed oil will greatly affect the use of aromatic extracts in printing inks as their greatest outlet in printing inks at present is in those inks that contain little or no linseed oil.

You must remember that when you print a sheet of paper, immediately after printing, or within two or three seconds afterwards, you put another sheet of paper on top, thereby quite effectively excluding the oxygen from the bottom sheet, which renders it difficult for the ink to dry by oxidation. Consequently, unless the paper is sufficiently absorbent for the ink to dry by penetration, the ink will not dry to a hard rub-proof film unless the oil used has good drying properties.

DR FRANK MORTON : In the first table in the paper, showing the properties of some petroleum solvents used in photogravure inks, the solvents referred to are obviously benzene, toluene, and xylene concentrates. What is known concerning the toxic effects of these solvents, particularly the apparently greater toxicity of benzene as against xylene and toluene, and to what extent is the printing ink industry likely to require replacements of benzene concentrates by concentrates boiling in that range, but not containing aromatics?

I should like to ask whether or not the utilization of certain petroleum fractions in printing inks has resulted in carcinogenic effects. Also to what extent has the dermatitis which occurs in the printing industry, particularly among the litho people, been laid at the door of petroleum products as against the resins and varnishes used?

To what extent does the introduction of the new plastic rollers in the rotary offset machines in the States affect the use of petroleum products in the inks, especially as I was told recently that the rollers were likely to be affected by aromatic solvents?

DR HEALEY: The question with regard to the rollers is fairly complicated. Several different materials are used for making rollers for printing presses, and I think you would say that generally speaking they have a somewhat limited life; we tend rather to ill-treat them by the things we put into the inks. Rubber rollers in particular, of course, are affected by mineral oils. We also put in cobalt driers, which are very deleterious. I do not know that I am familiar with the particular rollers to which Dr Morton refers; but I think the general position is that the majority of rollers have a reasonably long life having regard to the types of inks with which they are used.

I have never heard of any printing inks producing trouble owing to their carcinogenic effects. I do not think it is very likely because, if you look at any of the samples I have exhibited here this evening, you will note that they are very messy materials; and one does not handle printing inks more than one has to. If there is any effect of that sort I should think it is more likely to be a dermatitis effect due to the solvents used for your hands afterwards. I cannot recall a single definite case in which that has occurred, however. I think the majority of industrial diseases that occur in the printing trades as a whole come from lead poisoning, particularly in connexion with the casting of lead alloys for making type.

The point in regard to the toxicity of benzene as against that of xylene and toluene is that in all progressive photogravure works they use solvent recovery plant and do not permit a dangerous concentration of solvent vapours to occur. Normally the smaller plants, which do not take such precautions, would use the much-slower-drying solvents, because the Factory Regulations would not permit the use of benzene and toluene in such circumstances. Benzene and toluene would be permitted only where special precautions are taken, as in many modern plants which are coupled with a solvent recovery apparatus. I do not think that the amount of benzene vapour in the majority of photogravure shops would reach anything like toxic proportions.

DR MORTON: I think recent investigations have shown that the toxic effect of benzene is particularly marked, and that over a long period of time it is ultimately fatal.

DR HEALEY: I believe that is true; but I have never heard of any case of benzene poisoning in any photogravure plant.

DR MORTON: I think that cases have been reported within the last

two or three years. There have been questions by Medical Officers as to whether the statement that that is the cause of death is correct.

DR HEALEY : If benzene is used, and if adequate precautions are not taken for its removal, it may have that effect. But I think that in the majority of plants the precautions taken are adequate.

DR MORTON : In your opinion is it necessary for the manufacturers in the petroleum industry to consider making a light volatile product which does not contain benzene; or would a benzine fraction be suitable?

DR HEALEY : I think a benzine fraction would be suitable, although a fraction without benzene, provided it is a suitable solvent for the resins used, would be more suitable.

DR MORTON : Do you recommend it?

DR HEALEY : If it is suitable for the resins used, I think it could be employed.

MR J. A. L. HAWKEY : The question has been raised by Dr Zaky as to whether petroleum products, and particularly petroleum extracts, are being used only by reason of the shortage of linseed oil. At least ten years ago I was bold enough to predict that within ten years from then linseed oil would be of minor interest in printing. I still think that that will be the case, for we are not getting all the linseed oil we want at the moment, and the probability is that we shall not get all we could want for some years to come; so that it is up to us to try to replace it. In order to do that we have to consider what we want in these substitutes, and as an ink maker I confess that we ourselves are not perfectly clear. It is true to say that much of the linseed oil that is being replaced will never be required for the same purpose. In quite a number of formulations we can actually obtain better results by leaving out linseed oil.

Another point bearing on that is the degree to which one type of printing will advance at the expense of another. We are not altogether clear in our minds about that. But that will have a very big influence, of course, on the types of materials used in the largest proportions in printing ink manufacture.

My own particular difficulties come about because I am mainly concerned with lithographic inks, where we have to consider affinity for water, and where all the factors concerning pigment wetting favour emulsions. If the petroleum industry wants to satisfy the printing ink industry there must be much closer contact; they will have to discuss together what is really required. We must not merely omit linseed oil and put in something else in the hope that we shall achieve what we want; we must be perfectly clear about the requirements, and if we are clear about them I think the petroleum industry will be able to provide them.

MR P. KERR : Perhaps Dr Healey has some information to give on the difficulties he has experienced with petroleum products.

DR HEALEY : I do not think I have a great many points to raise in that connexion. Before the war I was beginning to get quite interested in some of the close cut fractions which the petroleum industry were just beginning to supply, in particular one having a boiling range of 260° to 290° C, which is no longer available. I think that to some extent some of these closer cut fractions might be of great use to us, particularly if heat-drying inks of the vaporin type come into use in Great Britain.

THE CHAIRMAN : I am surprised that some ink makers have not challenged Dr Healey's statement that carbon black is the ideal pigment for printing inks. It has the disadvantage, as indicated in the paper, that it confers some unpleasant rheological properties on inks. Whether or not those rheological properties are inherent in carbon black I do not know; possibly the petroleum people may have some observations to make on that matter. But suspensions of carbon black used in printing ink are thixotropic, introducing all sorts of difficulties in use and requiring complicated inking mechanisms to be incorporated in printing machines.

DR HEALEY : You rather criticize my statement that carbon black is the ideal pigment for printing inks. Perhaps I did put it a little too strongly. I suppose no pigment is ideal; perhaps I should say that carbon black has more virtues than the majority of other pigments. The difficulties due to its rheological properties I think we are usually able to cope with fairly well; I agree that sometimes we have difficulties, but we are usually able to get over the absorption of driers and that sort of thing. I would not say that the rheological properties of some of the other pigment dispersions we use are quite all that they might be.

MR P. KERR : Should we attribute the rheological properties of a suspension of carbon black so completely to the carbon black itself? Might these not be modified by the presence of other substances?

As regards the production from petroleum of special cuts to take the place of benzole, much would depend on how many of the incidental properties of benzole it was desired to retain. It might be difficult to produce relatively small quantities of special products on plants of relatively large throughput.

MR F. J. S. HALL : It is stated in the paper that greases are sometimes used to shorten the ink and to remove excessive tack. A little later it is stated that the use of too much grease is undesirable owing to the greasy stain caused at the back of the paper and to other deleterious properties. I wonder how far the printing ink trade has asked for the co-operation of the petroleum grease manufacturers, because greases can be made, of course, from almost any type of oily liquid and almost any type of metallic soap base. For instance, even drying oils could be employed or the very same vehicle as used in the manufacture of the ink. The properties of the grease can therefore be varied very considerably to meet any particular need. Bearing all that in mind, it is practically certain that, given proper co-operation and research into the problem, greases could be made which would not give rise to all the difficulties mentioned in the paper. I should welcome comments on that matter.

DR HEALEY : Probably the case mentioned by Mr Hall is not the only case in connexion with which the ink maker might co-operate more with the manufacturers of the various raw materials. There are certain difficulties, however, in the particular case of greases. If we can obtain the effect we want, as is usually the case, by the addition of a comparatively small amount of grease, we are quite happy. I mentioned that if an excessive amount of grease is added, various other effects are manifest, but I did not explain why that is so. Usually greases are added to inks with a linseed oil or other drying oil basis. An excessive amount of grease, or for that matter petroleum jelly or other non-drying material which might be added to reduce the tack, by virtue of the fact that it is non-drying will slow down the drying of the ink. If, during the time the ink is drying, when it is in the comparatively liquid state, or at any rate when a proportion of the vehicle is in the liquid state, there is an excess of grease present, the tendency will be to stain through the paper. The addition of practically any non-drying material, no matter how it is compounded, will have that effect.

Speaking as a printing ink maker, I aim to make inks which will print satisfactorily, and not to use the largest possible amount of grease in those inks. Usually the addition of 3 per cent, or perhaps at the most 5 per cent, will do the job. An excessive amount will probably reduce the tack of the ink to the extent that it will not transfer from one roller to another; it will slow down the drying, and that will cause various other difficulties. I am not in any way blaming the grease manufacturers for giving us a grease which will cause a stain on the back of the printed paper, if we are putting 50 per cent of grease into an ink; it would be our fault for putting in so much. The use of greases containing drying oils may be developed particularly in some specialty inks.

MR HALL : Greases are derived from so many sources that I think you can alter the properties in order to obtain what you want.

MR S. E. A. MOON : With regard to the thixotropic effect of carbon black in suspension, I have not had experience of it in printing inks, but in nearly all suspensions of carbon black such an effect is apparent. Unfortunately, it is an inherent property of the material, and I have always suspected it to be due to very high molecular weight hydrocarbons left in during manufacture. To overcome the difficulty, surely some adjustment of the solvent could be made, such as by the addition of a de-flocculant solvent to the ink.

About the dermatitis effect; invariably when dermatitis occurs due to any material it is said that it must be due to the petroleum solvent. In my experience, the petroleum solvent does not cause and never has caused dermatitis; but unfortunately the solvent action lays the skin open to dermatitis effects from other materials. There are various treatments, however, which will overcome that difficulty.

I would point out that the first table in the paper, giving the properties of some petroleum solvents used in photogravure inks, does not refer to aromatic products; they are petroleum fractions. . . .

MR F. MORTON : They have as much as 43 per cent aromatics.

MR MOON : Yes, but presumably they are obtained from the petroleum.

THE CHAIRMAN : I should like again to express our very sincere thanks to Dr Healey and Dr Ivanovszky for their very interesting paper. I must repeat that I think lectures of this kind are much to be encouraged, in that they bring together two industries, one of which uses the products of the other; only good can possibly arise from such discussions by the technical people concerned.

For that reason we of the printing ink industry are grateful to the Institute of Petroleum for having arranged this paper and meeting, and we are all grateful to the authors for the work they have put into the paper. I am sure those of the printing ink industry will agree with me that the list of the uses of petroleum products in our industry as compiled by Dr Healey and Dr Ivanovszky is very comprehensive indeed. So far as I can see, nothing has been omitted. That is another indication of the care which has been devoted to the preparation of the paper. The experience behind it is very considerable, and the paper is one to which we can refer in the future, knowing that it is authoritative.

I express to you, Dr Healey and Dr Ivanovszky, our very warm thanks for a most enjoyable and instructive evening.

(The vote of thanks was carried with enthusiasm.)

DR HEALEY : I should like to thank you all very much for your very kind reception. I also take the opportunity to thank the various firms and individuals who have helped us with the samples that we have displayed for your interest. There are also some examples shown of different types of printing which you may like to examine.

In conclusion I may recall an incident which occurred on my entry into the printing ink trade. The technical director of a very large cable company, which employed a considerable number of technical people at that time, said to me : " Printing ink ? You want to make printing ink, just mixtures of carbon and oil ? " I have not seen him since ; but, having found out all the other things which go into printing inks, if ever I do meet him I will ask if he is still making cables, just wrapping paper around wires !

On the motion of Mr Jackson, the warm thanks of the meeting were accorded Dr Riddell for the manner in which he had presided over the meeting.

THE OXIDATION OF TRANSFORMER OIL.

By P. M. HEERTJES, C. D. TEN HAVE, and J. J. LOCK.*

SUMMARY.

With the object of obtaining some information as to the mechanism of the ageing of transformer oil, measurements of the dielectric losses occurring on oxidation were made. The acid, saponification, and hydroxyl numbers, etc., of the oil were also determined, as well as the amounts of water, carbon dioxide, and volatile products, formed during the oxidation.

INTRODUCTION.

BRUCKMAN^{1, 2, 3} has constructed an apparatus in which transformer oil can be aged in 100 hours to the same extent as in 15 to 20 years of normal use, and this apparatus also records automatically the dielectric losses occurring during the oxidation.

The accelerated ageing is achieved by passing through the oil, at 100° C and in the presence of copper as catalyst, a stream of dry, carbon dioxide-free, oxygen at the rate of 1650 ml (standard condition) per hour per litre of oil. During the process the oil is subjected to 10,000 volts A.C. and the dielectric losses are measured at the increase in the angle of loss $\tan \delta$, which is recorded automatically.

This research was extended to the inclusion of other gases, such as nitrogen, and it was considered important to determine as far as possible the chemical changes in the oil. Therefore, while passing the different gases through a transformer oil in the Bruckman apparatus, not only was the change in $\tan \delta$ determined but also the change in such properties of the oil as acid, saponification, and hydroxyl numbers, and in the amounts of volatile organic products, carbon dioxide, and water. As far as possible the conditions of the normal experiment were maintained.

Although the results are not sufficient to give a clear picture of the reactions which occur during the ageing of transformer oil, the authors feel that they give some data to workers in this field and will provide a basis for criticism.

THE BRUCKMAN APPARATUS.

The ageing apparatus (Fig. 1) consists of a heat-resisting glass vessel, of about 2-litre capacity, provided with a connexion for high tension current. The top is a ground fit on the vessel and carries, by means of two bolts, a mica-glass composition block to which the parts of the copper condenser are fitted. Gas is introduced through one of the bolts, which is hollow. This gas agitates the oil and, if oxygen is used, ages it. The condenser is connected to the recording apparatus and the vessel stands on an electric boiling-plate, auxiliary means of heating being also provided. Temperature is regulated to $\pm 0.1^\circ \text{C}$ by means of a relay in the auxiliary heating system and is controlled by a contact thermometer placed in the oil.

* Chemical Engineering Laboratory, Technical University, Delft, Holland.

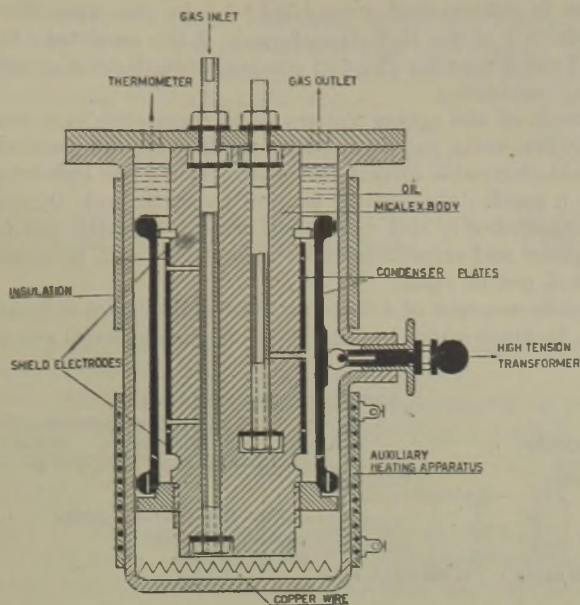


FIG. 1.

BRUCKMAN AGEING APPARATUS.

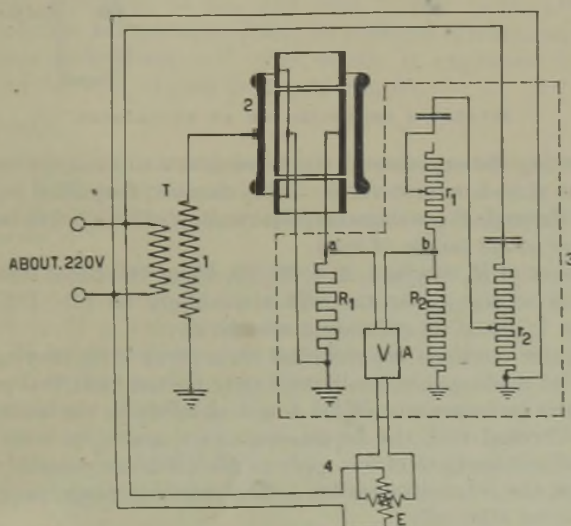


FIG. 2.

DIAGRAM OF AUTOMATIC RECORDING APPARATUS.

If oxygen is used as the gas, the influence of heat and the presence of the catalyst causes the oil to age rapidly. During this ageing $tg\delta$ increases and

this increase is automatically recorded^{3, 4, 5} by the apparatus shown in Fig. 2, in which 1 is the H.T. transformer, 2 the condenser in the ageing apparatus, 3 the intensifier (V) and compensating tension generator, and 4 the recording wattmeter.

One electrode of the ageing apparatus is connected to a source of A.C. current at 10,000 volts, the other being earthed via the resistance R_1 , with the two shield-electrodes directly earthed. When the current flows, point a will have a small difference in tension to earth and, through the condenser and resistance r_1 and r_2 , a small tension to earth can be generated at b . The phase and amplitude at b can be varied and, in general, voltages at a and b will not be equal.

At the commencement of a determination the tension at b can, by means of r_1 and r_2 , be made equal to that at a . If the electrical properties of the

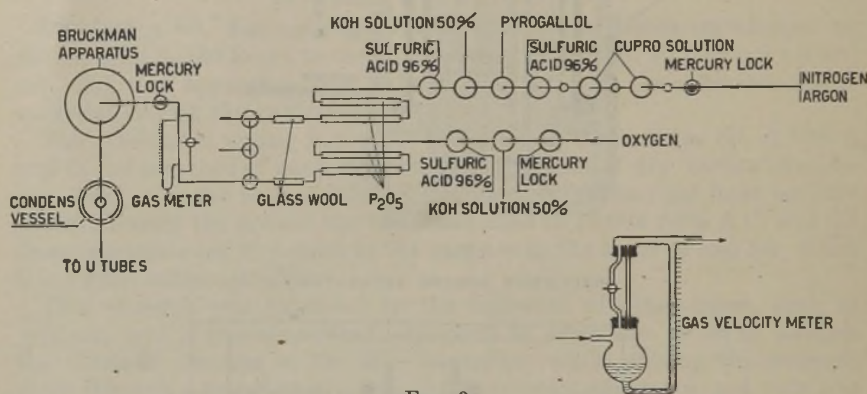


FIG. 3.
APPARATUS ARRANGED FOR AN EXPERIMENT.

oil change during the experiment the tension at a will change and a current will flow from a to b or vice versa. This current, magnified by the intensifier, passes through the wattmeter, the reading of which will be a measure of the increase of $tg\delta$ (angle of loss).

The resistance of R_2 can be 1, 2, 4, 10, 20, 40, or 100 times that of R_1 , and the sensitivity of the apparatus will accordingly be $1/1$, $1/2$, $1/4$, $1/10$, $1/20$, $1/40$, or $1/100$ of its maximum sensitivity.

The wattmeter readings are recorded on a paper strip moving at 0.5 cm per hour. The readings are qualitative only for the electrical properties of the oil, and the measurement of $tg\delta$ is not absolute as the wattmeter scale cannot be calibrated with the adjustments of r_1 and r_2 or with changes in frequency and voltage in electric supply. Also, it is not possible to calibrate the scale from the intensifier values. The absolute magnitude of $tg\delta$ can only be measured statically.

Auxiliary Apparatus.

By means of the auxiliary apparatus shown in Fig. 3 it is possible to use oxygen or nitrogen, the latter being freed of oxygen by means of a cupro solution in ammonia in which free copper is present, and a solution of

pyrogallol. The cupro solution was made by mixing 1 part concentrated ammonia (density, 0.9), 1 part water, and 1/20 part Cu_2Cl_2 . The solution was saturated with NH_4Cl . Oxygen content of the nitrogen used was determined according to Mugdan and Sixt.⁶

ANALYTICAL METHODS USED.

Acid Number.

This was determined in the usual way by titration with 0.1N alcoholic potassium hydroxide and the result expressed as mg KOH needed to neutralize 1 g of oil.

Saponification Number.

Found by saponification with 0.5N alcoholic potassium hydroxide and the result expressed as mg KOH used per gram of oil.

Before determining acid and saponification numbers the oil was dissolved in 50 ml indicator solution prepared by dissolving 1 g alkali blue 6B in 600 ml benzene and 400 ml alcohol.

Hydroxyl Number.

The method of Normann-Schildknecht⁷ as improved by Kauffman⁸ and Gorbach⁹ was used. After acetylation with acetic acid anhydride the reaction mixture was dissolved in 50 ml of indicator solution before titration.

Hydroxyl number is expressed as mg KOH per gram of oil.

Peroxide Number.

Determined according to the Jule and Wilson method,¹⁰ the titanio trichloride solution being prepared and its strength determined as described by Waterman and Heertjes.¹¹ The result is expressed as milligram equivalents of reactive oxygen per kg of sample.

Carbonyl Number.

For determining the amount (in mg) of potassium hydroxide needed to neutralize the hydrochloric acid liberated during the reaction of 1 g of oil with excess of hydroxylamine-hydrochloric acid, the following method was developed. See also 12

About 4 g (*P*) of the sample is weighed accurately in a 150-ml Erlenmeyer flask and dissolved in 50 to 60 ml of a solution containing 600 ml benzene, 400 ml alcohol, 25 g hydroxylamine-hydrochloric acid, 25 mg dimethyl yellow, and 25 mg bromophenol blue. To this is added exactly 10 ml of about 0.5N alcoholic potassium hydroxide and the solution boiled for 3 hours under reflux. After cooling it is titrated with a 0.1N alcoholic hydrochloric acid solution until an orange yellow colour ($\text{pH} = 3.0$) appears. If for this titration *a* ml of N hydrochloric acid are used, and for a blank solution similarly treated *b* ml are used, the carbonyl number is given by the formula :

$$\frac{56.08 (a - b)N_{\text{HCl}}}{P}$$

Volatile Products.

The gases leaving the apparatus are passed through a calibrated vessel, cooled by a solid CO_2 -alcohol mixture, in which all the volatile products

except CO_2 are condensed. The products separate into oil and water layers, the amounts of which are recorded.

The CO_2 is measured by passing the gases from the condenser through two U-tubes containing soda-lime.

Condenser and U-tubes are duplicated for alternate use to facilitate continuous operation.

Dissolved Gas.

The volume percentage of gas dissolved (in gas percentage at 0°C and 760 mm) in the oil at the temperature of the experiment is determined in

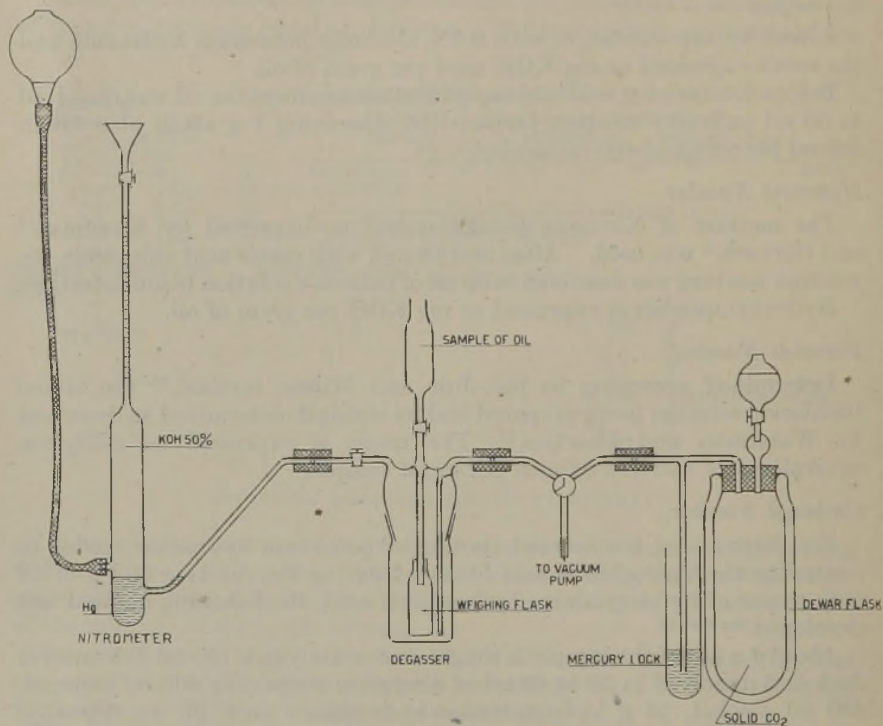


FIG. 4.

APPARATUS FOR DETERMINING AMOUNT OF GAS DISSOLVED.

the apparatus shown in Fig. 4. The use of a Dewar flask¹³ to produce pure CO_2 is considered to be the best and safest method, as that obtained by means of the Kipp's apparatus always contains other gases.^{14, 15}

The apparatus is similar to that used by Clark¹⁵ to determine gas solubility in transformer oil. Before introducing the oil, care must be taken to ensure that the apparatus is free from air by washing with CO_2 and evacuation. The oil is introduced in droplets and degassed under vacuum. The weight of oil is determined by weighing the small flask and the dissolved gas is driven into the nitrometer by the CO_2 .

OILS INVESTIGATED.

Five transformer oils of different grades from the same crude oil were available and three of these were used in the experiments. Their properties are given in Table I.

TABLE I.
Properties of Transformer Oils.

	Oil.				
	7370A.	7370B.	7370C.	7370D.	7370E.
H ₂ SO ₄ used in refining .	6%	13%	20%	40%	60%
Acid number .	0.05	0.05	0.05	0.05	0.05
Saponification number .	0.1	0.1	0.1	0.1	0.1
S-content .	0.2%	0.18%	0.18%	0%	0%
N-content .	0%	—	—	—	—
Naphthenic rings *	33.4%	33.6%	33.8%	34.5%	34.5%
Aromatic rings *	10.8%	9.0%	8.4%	3.9%	3.1%

* Determined by method of Vlugter-Waterman.¹⁰

EXPERIMENTAL PROCEDURE.

One litre of the sample is dried over Na₂SO₄, filtered, and placed in the Bruckman apparatus. A coil of thoroughly cleaned copper wire is placed in the bottom of the apparatus and the lid and other parts put in position. The oil is heated by means of the warming-plate and the auxiliary system for 45 minutes and in this period is degassed and dried by applying a vacuum of 3 mm mercury. When the temperature of the oil is constant at 100° C the drying is stopped and gas is introduced into the oil. The condenser and U-tubes and the automatic recording apparatus are connected and the high tension current is switched on. If the current were switched on during the degassing period the gas bubbles between the condenser plates would cause a break-through in the condenser.

If the wattmeter reading tends to become too high during an experiment the sensitivity of the intensifier must be reduced. It is not possible with the present apparatus to register the dielectric losses and at the same time draw samples. If acid, saponification, and hydroxyl numbers are to be determined during an experiment, the loose electrode is withdrawn from the apparatus and the high tension current and the intensifier are disconnected.

Before analysis all samples were degassed at 1 mm mercury and a suitable temperature as dissolved CO₂ affects titrations with alkali blue 6B.

EXPERIMENTAL RESULTS.

Experiments I to V.

The first five experiments were made to examine the influence of degassing, gas changing, etc., on ϵ and details are given in Figs. 5 to 9. In these figures the various operations are indicated; thus \downarrow sens. $\frac{1}{2}$ indicates the reduction of sensitivity at $\frac{1}{2}$; \downarrow N₂ denotes the introduction of nitrogen; etc.

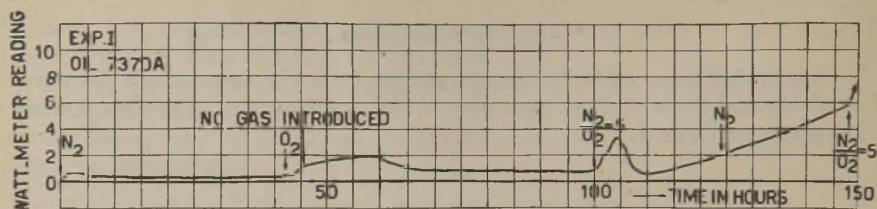


FIG. 5.

CHANGE OF $TG\delta$ WITH TIME FOR OIL 7370A DURING INTRODUCTION OF DIFFERENT GASES (EXPT. I).

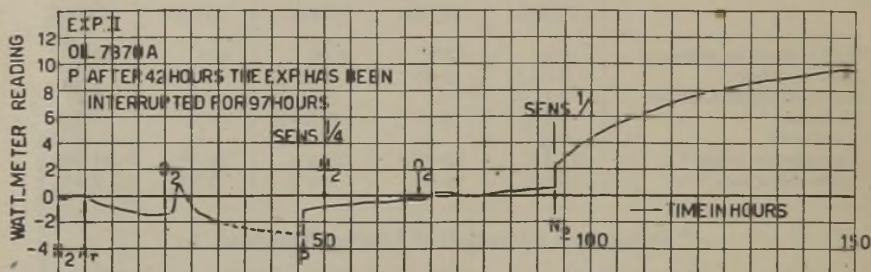


FIG. 6.

CHANGE OF $TG\delta$ WITH TIME FOR OIL 7370A DURING INTRODUCTION OF DIFFERENT GASES (EXPT. II).

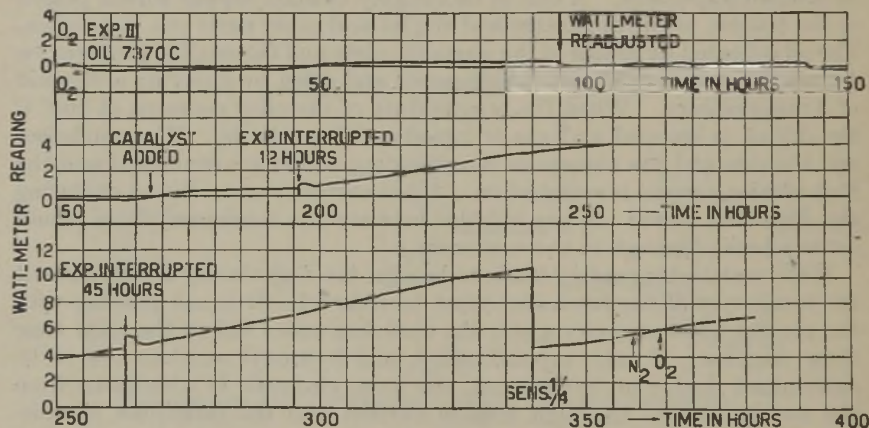


FIG. 7.

INFLUENCE OF CATALYST ON $TG\delta$ -TIME CURVE FOR OIL 7370C.

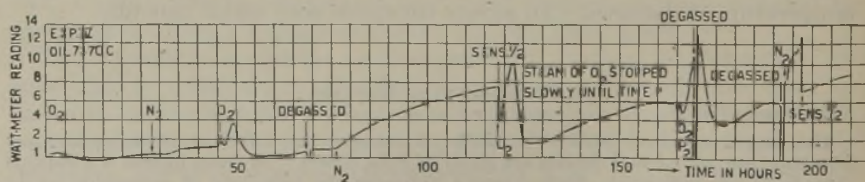


FIG. 8.

INFLUENCE OF DEGASSING ON $TG\delta$ -TIME CURVE FOR OIL 7370C.

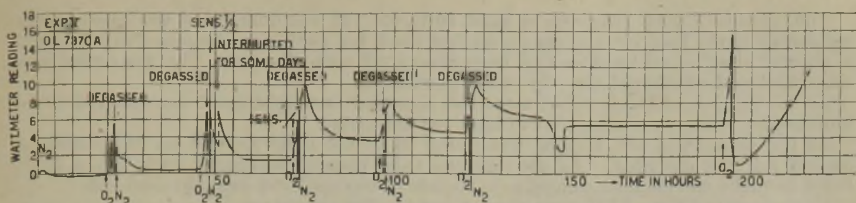


FIG. 9.

INFLUENCE OF DEGASSING ON TG δ -TIME CURVE FOR OIL 7370A.*Experiments VI to VIII.*

In these experiments the oil was treated continuously with oxygen and the gases leaving the apparatus were passed through a condenser and one U-tube containing calcium chloride and two U-tubes containing soda-lime. In experiment VIII 50 mg of copper stearate was used as catalyst instead of the copper coil.

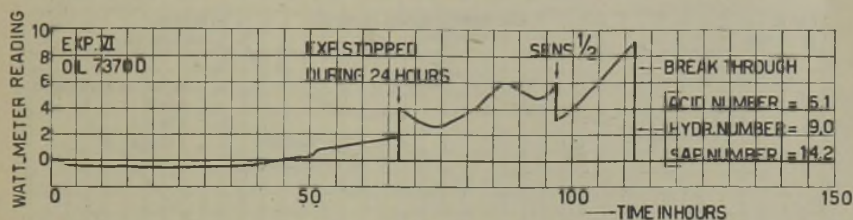


FIG. 10.

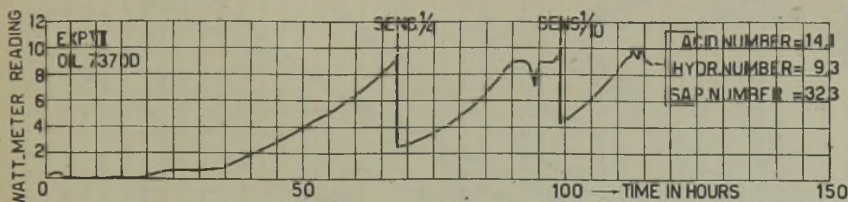
THE TG δ -TIME CURVE FOR OIL 7370D DURING TREATMENT WITH OXYGEN AND COPPER CATALYST.

FIG. 11.

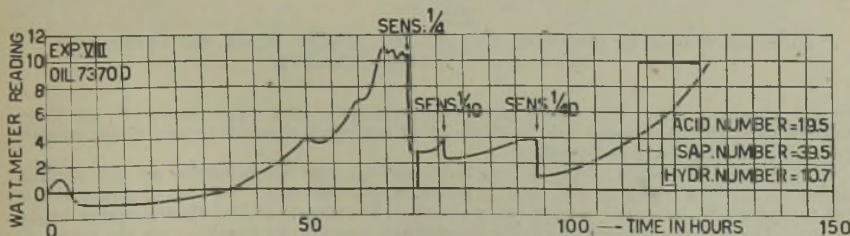
THE TG δ -TIME CURVE FOR OIL 7370D DURING TREATMENT WITH OXYGEN AND COPPER CATALYST.

FIG. 12.

THE TG δ -TIME CURVE FOR OIL 7370D DURING TREATMENT WITH COPPER STEARATE CATALYST.

The $t_{9\delta}$ -time curves are given in Figs. 10 to 12. It was found that the gases partly condensed in the long vertical gas outlet first used, but as this condensate was colourless it showed that no oil bubbles had been drawn off with the gas. The gas outlet was shortened and connected directly to the condenser.

As the calcium chloride tubes remained constant in weight they were proved to be unnecessary, and were discarded in later experiments.

As the amount of CO_2 formed was found to be too large for one set of U-tubes, a second set was installed. As soon as one tube became saturated with CO_2 a fresh tube, brought to constant weight in a stream of oxygen, was brought into use.

Experiments IX to XIII were carried out by this procedure.

Due to difficulties encountered in experiments VI to VIII, the quantity of volatile products and "water," although measured, are not recorded here. Acid, saponification, and hydroxyl numbers were determined at the end of each experiment and are shown on the figures.

Experiments IX to XIII.

These were normal ageing experiments using oxygen and the amounts of volatile products and CO_2 determined at regular intervals are shown in Figs. 13 to 17 in terms

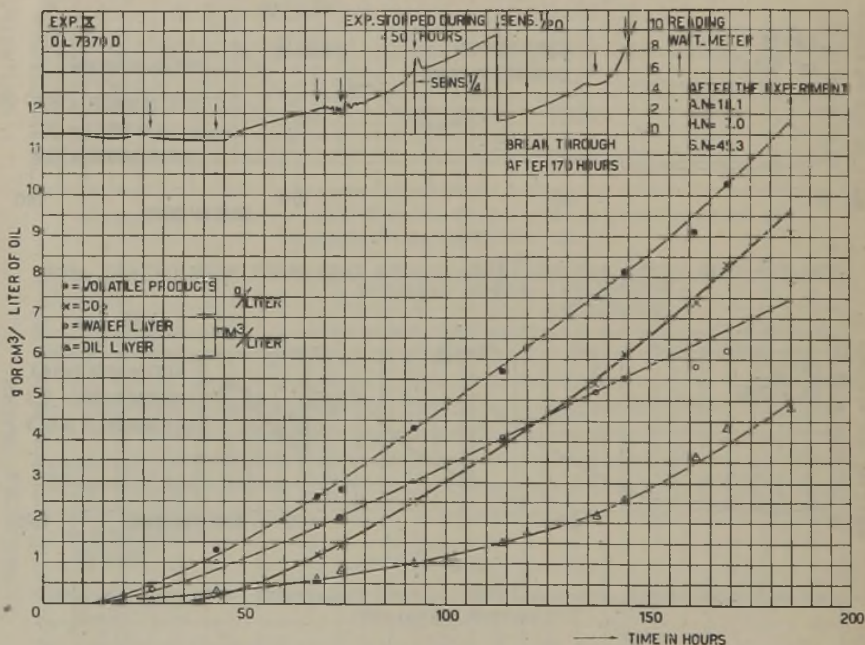


FIG. 13.

VOLATILE PRODUCTS OBTAINED DURING EXPERIMENT IX ON OIL 7370D WITH OXYGEN AND COPPER CATALYST.

of ml or g per litre, the latter being the quantity of sample used. From these experiments the conclusion can be drawn that no break-through occurs if the volatile products are regularly removed.

Experiment IX shows that a long interruption has no influence on the results, although $t_{9\delta}$ is affected as was seen in previous experiments. In this experiment the oil temperature became so high after about 170 hours that the thermometer broke down. On the assumption that this breakdown was due to sparking on the mercury reservoir, the high tension current was switched off after 162 hours in Experiment X. In Experiment XI, however, the thermometer again broke down after 140 hours, although no break-through in the condenser had occurred. The oil was boiling

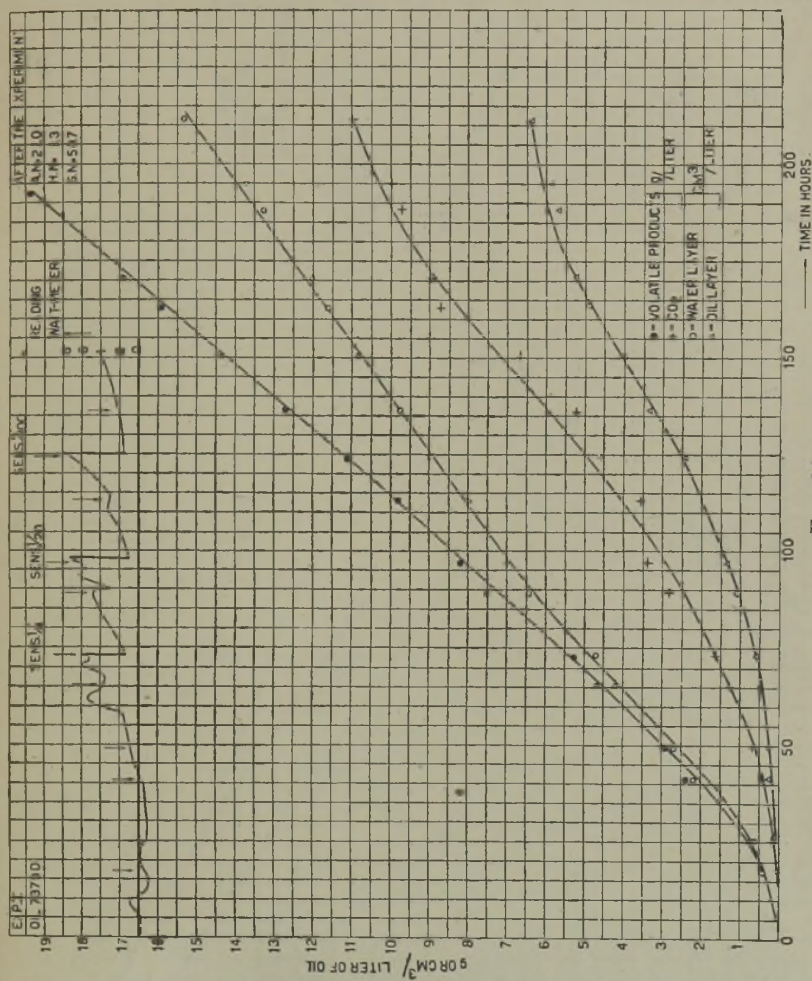


Fig. 14.

————— TIME IN HOURS.

Fig. 14. VOLATILE PRODUCTS OBTAINED DURING EXPERIMENT X ON OIL 7370D WITH OXYGEN AND COPPER CATALYST.

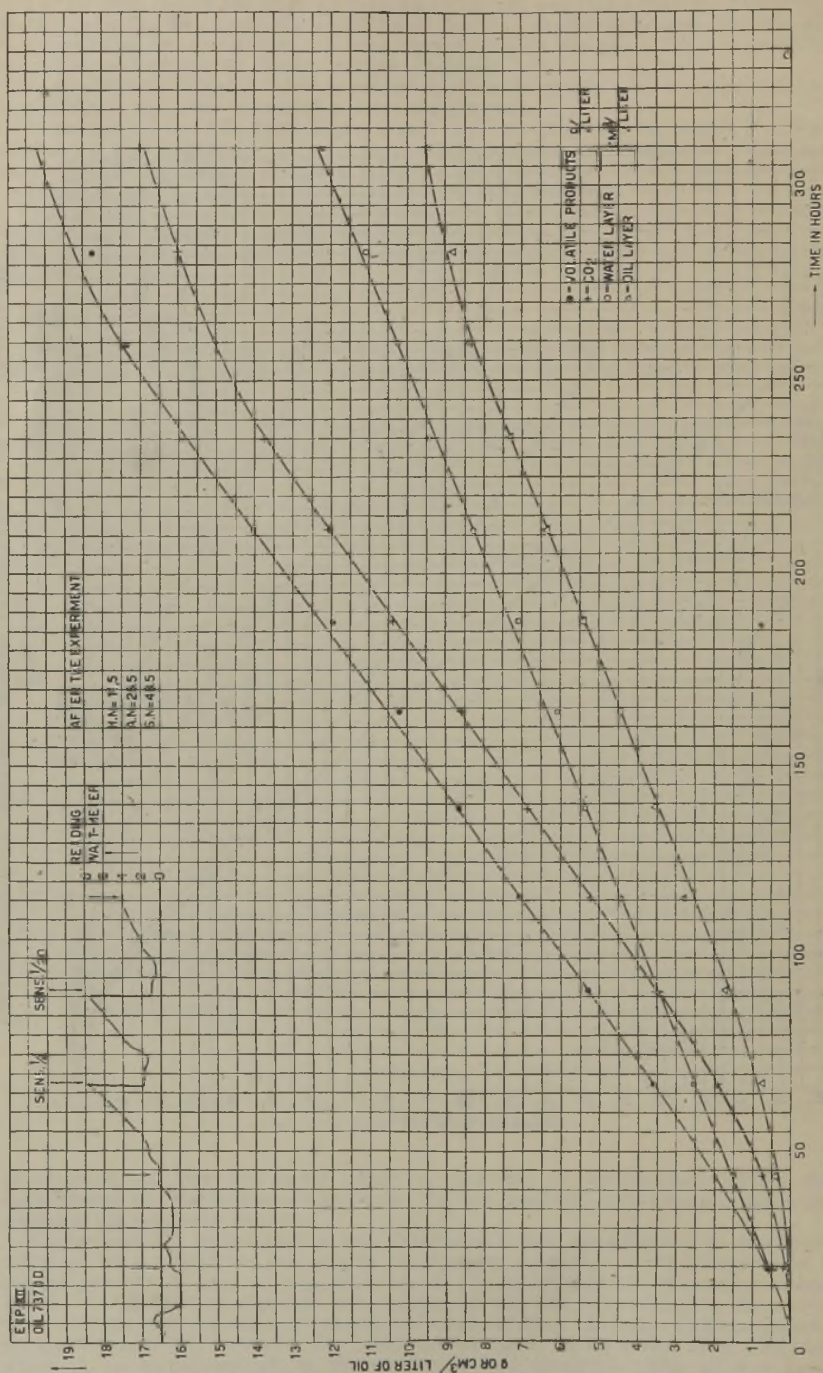


FIG. 15.

VOLATILE PRODUCTS OBTAINED DURING EXPERIMENT XII ON OIL 7370D WITH OXYGEN AND COPPER CATALYST.

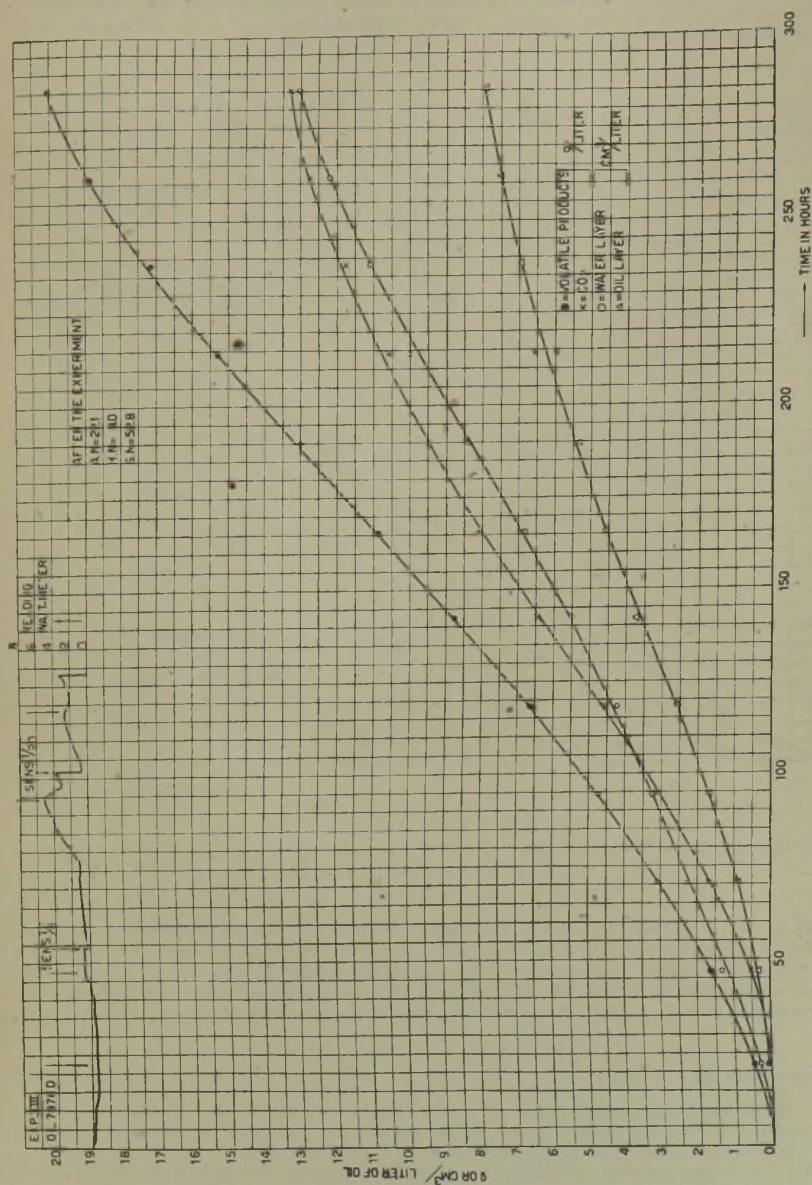


Fig. 16.

VOLATILE PRODUCTS OBTAINED DURING EXPERIMENTS XIII ON OIL 7370D WITH OXYGEN AND COPPER CATALYST.

rapidly and the wattmeter needle swinging violently. The experiment was stopped and when it was possible to open the apparatus the temperature of the oil was 300°C and it was partially carbonized. From this it can be concluded that the conductivity of the oil increased during ageing. High temperatures occur only during the last stages of the experiment.

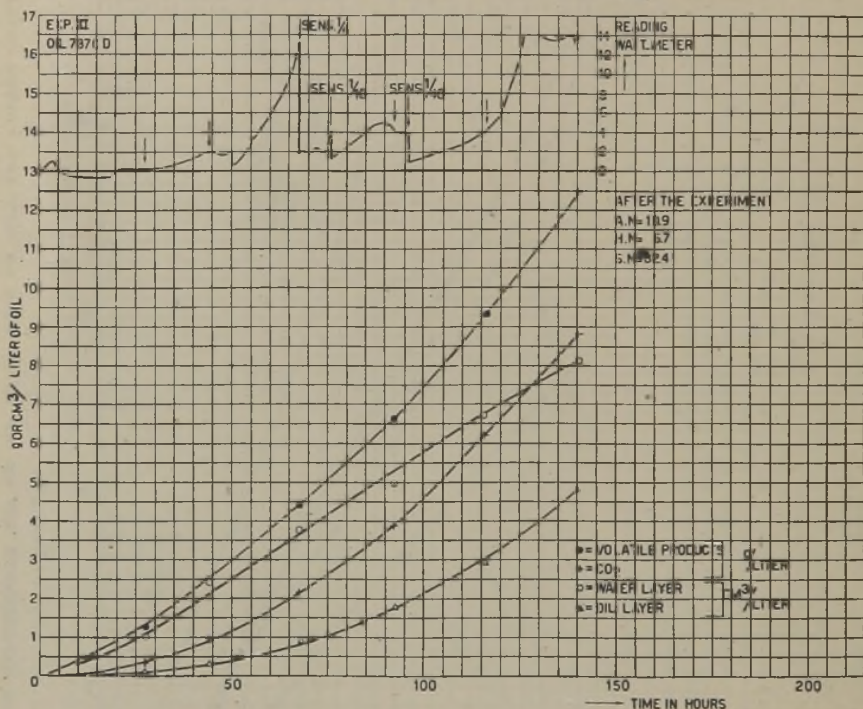


FIG. 17.

VOLATILE PRODUCTS OBTAINED DURING EXPERIMENT XI ON OIL 7370D WITH OXYGEN AND COPPER CATALYST.

As it was anticipated that the high temperatures had caused abnormal behaviour of the oil, Experiments XII and XIII were carried out as before but using a thermostat instead of a contact thermometer. Also, as soon as the increase of $tg\delta$ necessitated reducing the sensitivity of the intensifier to $\frac{1}{100}$ of its original value, the high tension current was switched off, thus preventing the temperature becoming too high.

Experiments XIV to XVI.

In these experiments the acid, saponification, ester, and hydroxyl numbers were determined during the ageing and in Experiments XV and XVI the peroxide number was determined also. The results are given in Figs. 18 to 20.

The Bruckman apparatus without the loose high-tension electrode was used in these experiments.

Experiment XVII.

The oil used in this experiment was pretreated with nitrogen in a sealed tube at 100°C for 625 hours. An ammeter was also placed between the transformer and the

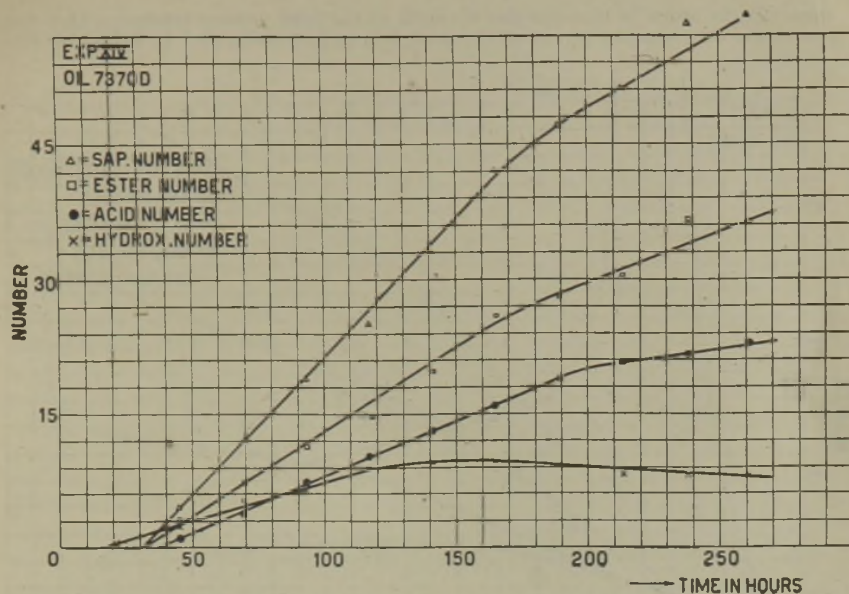


FIG. 18.

ANALYTICAL NUMBERS OBTAINED DURING EXPERIMENT XIV ON OIL 7370D WITH OXYGEN AND COPPER CATALYST.

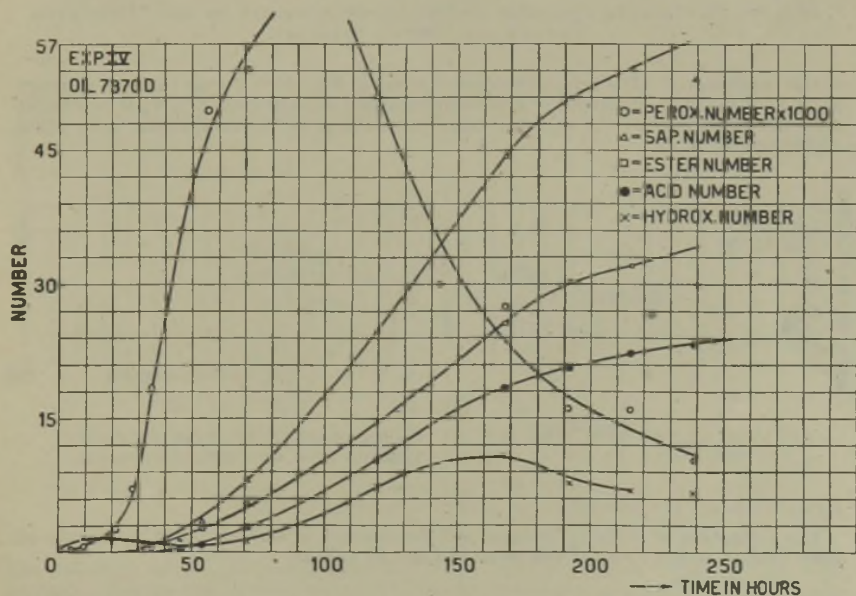


FIG. 19.

ANALYTICAL NUMBERS OBTAINED DURING EXPERIMENT XV ON OIL 7370D WITH OXYGEN AND COPPER CATALYST.

apparatus in order to measure the strength of the high tension current. This was practically constant at 0.65 mA at the start, but had increased to 1.48 mA at the end

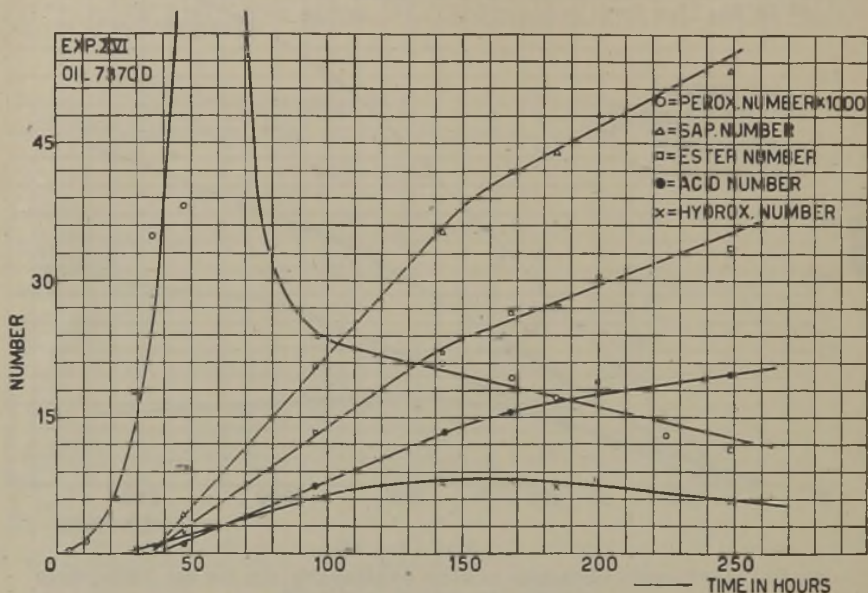


FIG. 20.

ANALYTICAL NUMBERS OBTAINED DURING EXPERIMENT XVI ON OIL 7370D WITH OXYGEN AND COPPER CATALYST.

of the experiment. The $t_{g\delta}$ -time curve is given in Fig. 21. Owing to some mercury having got into the oil, probably after degassing and changing over to N_2 , it is possible that the behaviour of the oil may have been abnormal in comparison with other experiments.

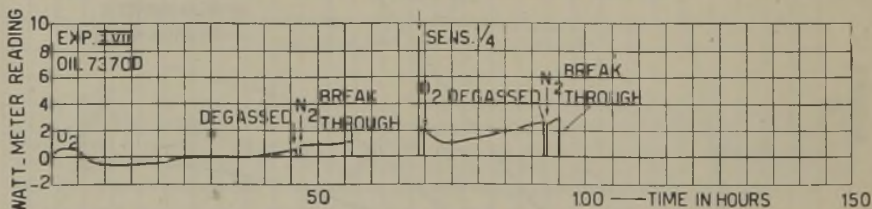


FIG. 21.

CHANGE OF $T_{g\delta}$ WITH TIME FOR OIL 7370D, PRETREATED WITH NITROGEN FOR 625 HOURS AT 100°C, DURING INTRODUCTION OF DIFFERENT GASES.

Experiments XVIII and XIX.

The formation of carbonyl groups and the amount of oxygen taken up by the oil were studied and the results are given in Figs. 22 and 23.

Experiments XX and XXI.

In these experiments the influence of nitrogen with 0.4 per cent oxygen was investigated. Initially the $t_{g\delta}$ only was measured in Experiment XX and, excluding

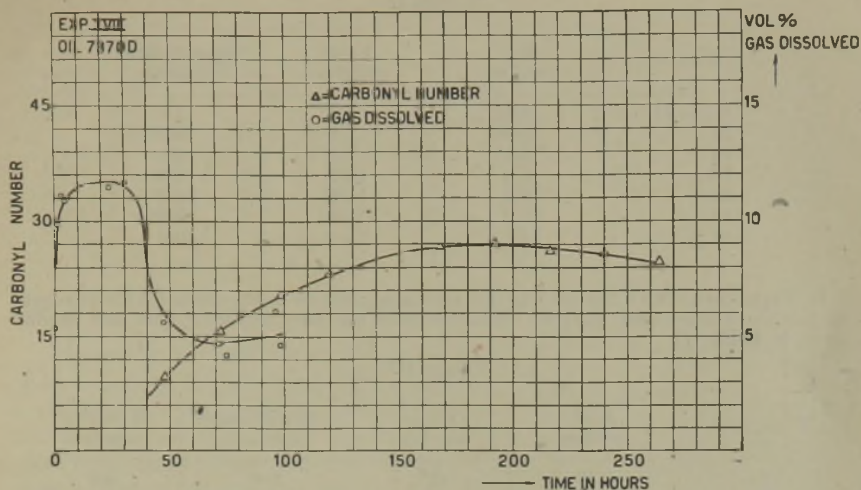


FIG. 22.

CARBONYL NUMBER AND GAS DISSOLVED IN EXPERIMENT XVIII ON OIL 7370D WITH OXYGEN AND COPPER CATALYST.

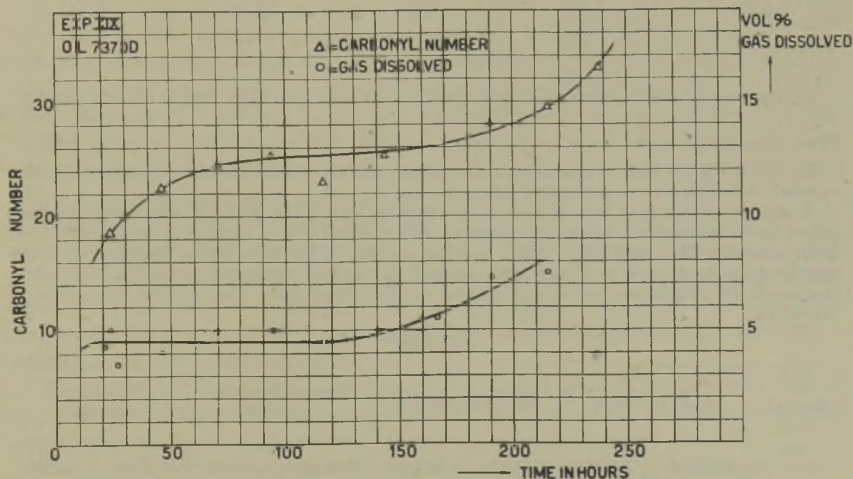


FIG. 23.

CARBONYL NUMBER AND GAS DISSOLVED IN EXPERIMENT XIX ON OIL 7370D WITH OXYGEN AND COPPER CATALYST.

the induction period, increased regularly with time but at a slower rate than with oxygen. Similar results were obtained with the first experiments with nitrogen only. After 740 hours, the nitrogen was replaced by pure oxygen, the determination of $tg\delta$ was stopped and samples were taken and analysed daily. The results are summarized in Table II.

TABLE II.

Time, hr.	Acid number.	Ester number.	Saponification number.
0 (= 740)	0.28	1.4	1.7
24	2.50	4.2	6.7
48	4.57	7.5	12.1
72	7.6	10.2	17.8
96	9.2	13.6	22.8
120	12.0	17.5	29.5
144	14.9	25.0	40.0

In Experiment XXI the η_{sp} was not measured, the oil being treated with nitrogen containing 0.5 per cent oxygen. Samples were regularly analysed with the results given in Table III.

TABLE III.

Time, hr.	Acid number.	Ester number.	Saponification number.	Hydroxyl number.
24	0.12	0.7	0.8	0.6
72	0.12	0.3	0.4	0.7
144	0.19	1.3	1.5	1.7
218	0.24	0.6	0.8	0.6
288	0.29	1.5	1.8	0.7
386	0.37	2.0	2.4	0.4
504	0.49	2.5	3.0	1.0
624	0.57	2.4	3.0	1.3
743	0.62	3.5	4.1	0.8
864	0.77	3.3	4.1	1.3
984	1.06	4.3	5.4	0.4

At the end of 984 hours the oil was dark red-brown in colour and perfectly clear.

Other Experiments.

In addition to the experiments described above, other investigations were also carried out with the transformer oils.

A sample of 75 ml of the oil from Experiments VII, VIII, and IX was sealed in glass tubes under nitrogen (excluding oxygen), and a small coil of copper wire was included with samples VIII and IX. After heating at 100° C for 850 hours, during which the oils became very dark in colour and a small amount of sediment settled in the tubes, the acid, etc, numbers were determined on the clear oil. The results are given in Table IV.

TABLE IV.

Sample from no.	Acid number.		Ester number.		Saponification number.		Hydroxyl number.	
	Before.	After.	Before.	After.	Before.	After.	Before.	After.
VII	14.1	13.1	18.2	18.2	32.3	31.3	9.3	7.1
VIII	19.5	17.2	20.0	25.6	39.5	42.8	10.7	8.0
IX	18.1	16.6	27.2	23.4	45.3	40.0	7.0	7.9

It was noted that, after storage for some months, the generally turbid oils from each ageing experiment became clear and a small amount of sediment had settled out.

Oils from Experiments XIV, XV, and XVI were stored for one year in flasks with normal cork stoppers, which permitted some contact of the oil with the air, and the acid, etc, numbers were determined with the results given in Table V.

TABLE V.

Sample from no.	Acid number.		Ester number.		Saponification number.		Hydroxyl number.	
	Before.	After.	Before.	After.	Before.	After.	Before.	After.
XIV	22.6	19.2	36.5	34.0	59.1	53.2	7.8	8.9
XV	23.2	19.4	29.8	32.7	53.0	52.1	6.6	10.2
XVI	19.5	18.0	33.6	26.2	53.1	44.2	5.8	9.4

CONCLUSIONS.

Regarding the behaviour of $tg\delta$ under different conditions Experiments I to V enable the following conclusions to be drawn.

Changing from nitrogen (freed as far as possible from oxygen) to oxygen causes the $tg\delta$ -time curve to take a peculiar shape, showing a maximum and a minimum after the introduction of the oxygen, the minimum being lower than at the moment the oxygen is introduced. This can be repeated.

When changing from oxygen to nitrogen the $tg\delta$ curve continue to rise rather sharply, but after a certain period the angle of inclination begins to decrease. It is probable that the increase in $tg\delta$ during the introduction of nitrogen is due to traces of oxygen in the nitrogen, as it has been proved that washing by the method described still leaves about 0.1 per cent oxygen in the nitrogen. It has been shown that pure nitrogen gives a flat $tg\delta$ -time curve,² and the same holds good for argon. The peculiar form of $tg\delta$ -time curve mentioned above is, after the first rapid increase, independent of interim periods of degassing when the high tension current is switched off. Moreover, the form is the same whether nitrogen or oxygen is introduced after degassing, except that if nitrogen is used and degassing takes place before the minimum in the curve is reached, this minimum is higher than if oxygen had been used. (See Figs. 8 and 9.)

If no copper wire is present with the oxygen the $tg\delta$ -time curve is flat and it can be concluded that the copper acts as a catalyst for the formation of oxygen compounds which cause the increase in $tg\delta$. The copper condenser plates are, or have become, inactive as a catalyst. It should be noted that the apparatus is cleaned by boiling in a benzene-ethyl alcohol mixture—strong acid, *e.g.*, is never used.

The cause of the peculiar phenomenon noted cannot be the reaction of O_2 with N_2 because if a change is made from Ar to O_2 the same shape of curve results.

During part of Experiments I and IV the stream of oxygen was accidentally cut off over-night. After readjustment to normal velocity the same maximum and minimum in the $tg\delta$ -time curve occurred. This also holds good for the start of an experiment and for nitrogen containing small percentages of oxygen. The behaviour of oils A and C is the same.

Experiments VI to VIII show that with pure oxygen the induction period read from the $tg\delta$ -time curves varies from 30 to 45 hours, with an average of 38 hours. Experiment VIII shows that the induction period is not controlled by the time necessary to dissolve a small amount of copper from

the copper wire and also that the copper stearate does not conduct electricity under the conditions mentioned.

Nevertheless, chemical reactions do occur during the induction period as shown by the formation, from the beginning of the experiment, of CO_2 , H_2O , acids (in the volatile products), peroxides (in the oils), carbonyl compounds (in the oils and volatile products) and hydroxyl compounds (in the volatile products).

In Fig. 24 all the hydroxyl, ester, acid, and saponification numbers, with the exception of those obtained during Experiments VI, VII, and VIII, are plotted as a function of oxidation time, the observations made while the oil was under high tension during the oxidation being marked by a circle around the point. The four lines were found by calculation.

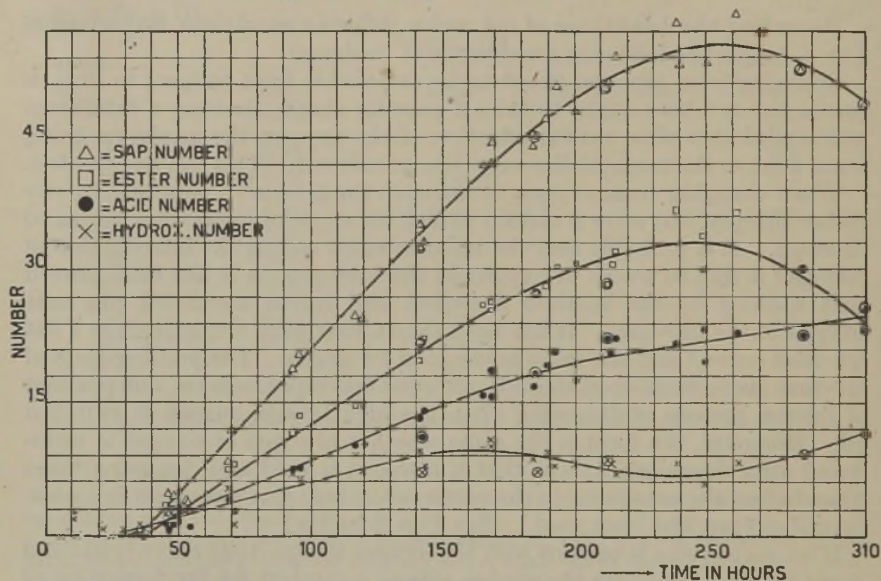


FIG. 24.

ANALYTICAL NUMBERS OBTAINED DURING TREATMENT OF OIL 7370D WITH OXYGEN AND COPPER CATALYST WITH AND WITHOUT HIGH TENSION TREATMENT.

From Fig. 24 it may be concluded that, apart from a small uncertainty regarding errors easily made in the determination of hydroxyl compounds, the acid, ester, and hydroxyl compounds are formed after an induction period varying from 36 to 40 hours. It is interesting to note that this period is equal to the period for the increase in $\text{tg}\delta$. It is likely that one of the compounds mentioned (probably the acid) is the cause of the increase in $\text{tg}\delta$.

It can be concluded from the experiments at moderate times (below 250 hours) that the electric field has no influence on the amount of hydroxyl compounds, acids, and esters. This warrants the use of determinations at about 300 hours as these strongly influence the shape of the lines.

After the induction period the ester, hydroxyl, and acid numbers increase linear with time.

After 150 hours the acid and ester numbers increase less rapidly, while the hydroxyl number decreases. This point coincides with the visible start of sludge formation (150 to 200 hours), the oil becoming dark and turbid and with sludge separation on standing. The quantity of sludge is small compared with the quantity of oil.

After this period the acid number again increases linearly with time, but more slowly, while the hydroxyl number continues to decrease and then increases. The increase in the ester number becomes slower and slower and then decreases. The hydroxyl-time curve reaches its minimum at practically the same point as the ester-time curve attains its maximum.

It is not possible to compare the experiments in sealed tubes at 100° C without free oxygen with the foregoing as the sludge has not been taken into account. Also, the change in acid, ester, and hydroxyl numbers is small and irregular. Copper appears to have no influence on these changes.

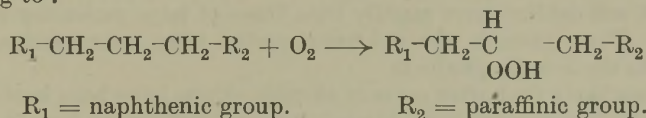
The differences in the experiments at normal temperature in cork-sealed flasks were also small and irregular.

In general it can be said that the compounds referred to continue to react with each other after their formation, forming for example sludge probably combined with copper.

All the data so far given indicate that the reactions and products are related to each other.

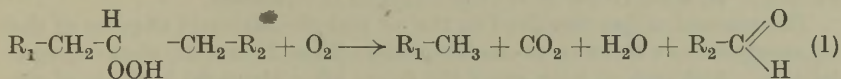
When it is remembered that peroxides (in the oil only), CO₂, H₂O, volatile products, in which large amounts of carbonyl compounds, acids, alcohols, and hydrocarbons (carbonyl number, 399.4; hydroxyl number, 61.1; acid number, 56.6; ester number, 49.5) are present are formed at once and that non-volatile acids, esters, and hydroxyl compounds are formed after a certain induction period, it seems that the following conclusions as to the mechanism of oxidation are warranted.

In the first place hydroperoxides are formed by the oxidation of the paraffinic side chains of the mainly naphthenic-paraffinic molecules according to:

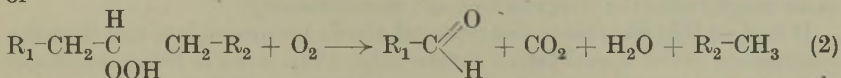


It may be noted that generally peroxides are considered to be the first-formed products of oxidation. (See 17, 18, 19.)

The hydroperoxides easily oxidize, giving rise to the formation of, *e.g.*, an aldehyde or ketone, CO₂, water and a hydrocarbon:



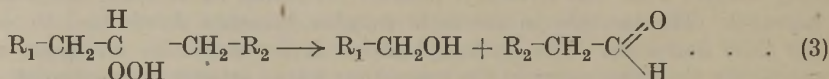
or



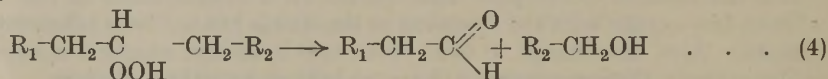
Because the oil and the oil layer of the volatile products both contain carbonyl compounds, whilst the oil layer contains hydrocarbons of low

molecular weight (Oxygen content : oil layer, 19.4 per cent; $\text{CH}_3-\text{C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{H} \end{smallmatrix}$, 36.4 per cent; CH_3OH , 50 per cent; butyric acid, 36.4 per cent; butanol, 21.7 per cent; etc.) it is clear that both reactions occur with reaction (1) prevailing.

At the same time the hydroperoxides can decompose according to :

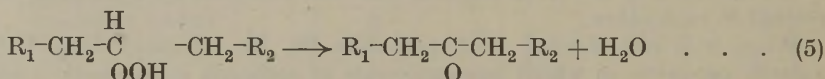


or



In this way carbonyl as well as hydroxyl compounds are formed. Because the amount of hydroxyl compounds in the oil is initially practically nil, reaction (4) occurs mainly although reactions (1) and (2) prevail above (4).

The hydroperoxides can still give rise to another reaction to form a ketone and water :



Comparing the amount of CO_2 and water found, bearing in mind that the water layer contains acids, it is not likely that reaction (5) will occur to any large extent.

After the formation of the carbonyl compounds they oxidize, forming acids, after which the hydroxyl compounds form esters with the acids. It is noteworthy that the induction period for the esters is longer than that for the acids. The low molecular weight carbonyl compounds in the volatile products will oxidize more rapidly than those of large molecular weight in the oil. Thus, even in the induction period some esters and acids are present in the volatile products.

It seems likely that after some of the side chains have been broken up in this way hydroperoxides of naphthenic structure will also be formed. These peroxides decompose to give ketones because the amount of CO_2 found after 250 hours of oxidation lessens in comparison with the amount of water.

After oxidation for 250 hours the amount of oxygen present in the compounds in the oil is about equal to that in the volatile products, viz, 25 g in each. In total 10 per cent of the oxygen is combined.

The amount of gas dissolved in the oil and the carbonyl number of the oil expressed as a function of oxidation time (Figs. 22 and 23) shown irregularities. Although in both cases the figure after about 60 hours is of the same magnitude, the irregularities are unsatisfactory.

It is clear that the researches reported above are incomplete and that the conclusions are of a qualitative nature only. The work is being continued and primary attention will be given to oxidation with low concentrations of oxygen. The isolation and analysis of the reaction products will also have major interest. In addition ring analysis and analogous methods will

be used for the unoxidized portions of the oil, whereas the oxidation products will be hydrogenated and the hydrocarbons formed will be analysed.

ACKNOWLEDGMENTS.

The authors desire to express their gratitude for the financial assistance rendered by the Delftsche Hoogeschool funds.

CHEMICAL ENGINEERING LABORATORY,
DELFT.
MARCH, 1947.

References.

- ¹ *Verslag N.E.C.*, 1942, 10.
- ² *Verslag N.E.C.*, 1943, 10.
- ³ *Confr. Inter. Gr. Reseaux Rapp.*, 1939, 105.
- ⁴ Bruckman, H. W. L. *Ingenieur*, 1937, **52**, E. 67.
- ⁵ *Confr. Inter. Gr. Reseaux Rapp.*, 1937, 108.
- ⁶ Mugdan, M., and Sixt, J. *Z. Angew. Chemie*, 1933, **40**, 90.
- ⁷ Normann, W., and Schildknecht, E. *Fettchem. Umschau*, 1933, **40**, 194.
- ⁸ Kaufmann, H. P. *Fette u. Seifen*, 1937, **44**, 150.
- ⁹ Gorbach, G. *Fette u. Seifen*, 1940, **67**, 505.
- ¹⁰ Yule, J. A. C., and Wilson, C. P. *Industr. Engng Chem.*, 1931, **23**, 1254.
- ¹¹ Waterman, H. I., and Heertjes, P. M. *Techn. Anaylsen*, IV, 89 (5e druk).
- ¹² Kaufmann, H. P. *Fette u. Seifen*, 1938, **45**, 618.
- ¹³ Kraus, R. *Z. Anal. Chemie*, 1943, **125**, 405.
- ¹⁴ Weygand, C. *Chem. Techn.*, 1943, **16**, 15.
- ¹⁵ Clark, F. M. *J. Franklin Inst.*, 1933, **215**, 29.
- ¹⁶ Waterman, H. I., and Leendertsen, J. J. *Techn. Analysen*, I, 188 (6e druk).
- ¹⁷ Discussion of Oxidation, Faraday Society, 1945.
- ¹⁸ George, P., and Robertson, A. *J. Inst. Petrol.*, 1946, **32**, 382.
- ¹⁹ Kreulen, D. J. W. *J. Inst. Petrol.*, 1946, **32**, 515.

A NEW METHOD FOR THE PRESENTATION OF TEST RESULTS ON THE FOUR BALL MACHINE.

By W. DAVEY, B.Sc., Ph.D., F.R.I.C.

SUMMARY.

The present method of presentation of results of tests on the four ball machine is discussed and a new method is proposed. It is suggested that the wear-load relation be expressed as a wear-load ratio, that the maximum load tested or determined be stated, and that the friction-time curves be referred to standard curves, observations on the type, occurrence and duration of seizure and of the maximum friction being given.

IN previous papers the present author has reported tests on the four ball machine in the form of detailed tables, and in the form of wear-load diagrams and friction-time curves, but it has been suggested that these methods of presentation of the results of such tests are unsatisfactory. With this suggestion in mind an attempt is now made to provide a more satisfactory method of presentation, to enable the reader to appreciate the results of a number of tests as quickly as possible, without sacrifice of essential data.

In order to appreciate the new method of presentation it is essential to discuss the results obtained from the machine and to explain their significance. The results obtained from each test on the machine are two in number; (1) the mean wear diameter, and (2) the friction-time curve. These two results are obtained for each applied load and the variation of frictional forces and wear over a series of loads constitutes the method used in the evaluation of a lubricant on this apparatus. The mean wear diameter is obtained by measuring the wear spots on the test balls and the early results obtained on the machine were represented graphically on log-log paper as a wear-load relation. It was found after a number of tests that there was no necessity to employ log-log paper and that a linear relationship between load and mean wear diameter exists for extreme pressure lubricants. It was also found that such curves for E.P. lubricants often showed one or two sharp breaks, since shown to be due to the E.P. additive in the oil reacting chemically with the test balls and thus functioning as a true E.P. additive. These sharp breaks in the wear-load diagrams correspond in most cases to the onset of sharp or instantaneous seizure, although the wear decreases after such a break. It is therefore essential, in any representation of the wear-load relation, to indicate such a break or change in the relation, since the load at which the change occurs may be regarded as the critical load at which true E.P. properties are first shown. It is proposed to replace the present wear-load diagrams with a wear-load ratio, which may be defined as the load (in kg) per mm of mean wear. It is important to realize that where a break in the wear-load diagram occurs two wear-load ratios are necessary to completely define the wear-load relationship. These two ratios, and the load at which the break occurs, will therefore be given.

Furthermore, in using a wear-load ratio, it is essential to indicate the

maximum load tested or which can be carried by the lubricant, since, without this, two oils, of vastly different E.P. rating, but having the same or similar wear-load ratios, may be assumed to possess similar E.P. properties. For this reason the maximum load tested or which can be carried by an E.P. lubricant will be given.

The friction-time curves, obtained as a direct record of the performance of the lubricant under test at a particular load, give valuable information on the performance of E.P. lubricants. These curves must be considered as complete accounts of the performance of a lubricant. Blok,¹ considered that the performance should be rated on the $2\frac{1}{2}$ sec seizing load, i.e., the load at which seizure occurs after $2\frac{1}{2}$ sec, but this method of assessment is of little or no value for blends containing reactive sulphur which show no sharp seizure even under extremely high loads. It has been found that additives of similar chemical composition and action exhibit similar friction-time curve characteristics and that certain of these characteristics are found in the curves of most good E.P. lubricants. On this basis it is proposed to classify these characteristic curves and to use this classification for reference purposes. For this classification the curves are conveniently divided into the following main types :

Type A. Straight Mineral Oil Type.

This type of curve (Fig. 1) is characteristic of straight mineral oils and shows a delayed seizure at low loads, with a high frictional torque and almost instantaneous seizure at loads of 100 kg, the period of seizure being prolonged and wear high.

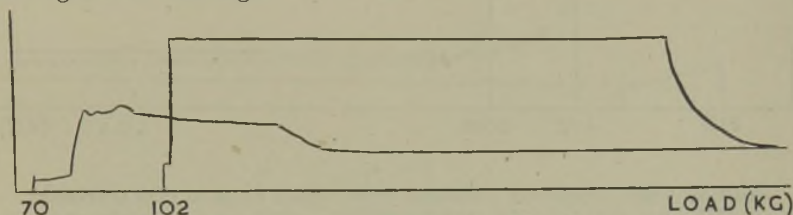


FIG. 1.

FRICTION-TIME CURVE FOR STRAIGHT MINERAL OIL TYPE (PENNA 150 NEUTRAL) OF E.P. LUBRICANT.

Type B. Oleic Acid Type.

This type (Fig. 2) is characterized by almost instantaneous seizure, even at low loads, with considerable variation in the frictional torque.

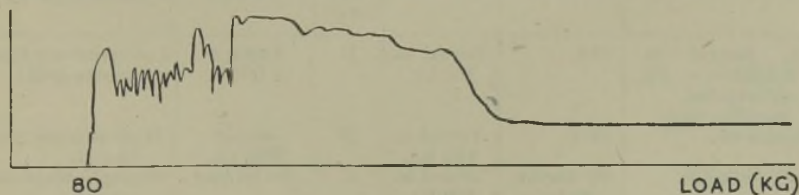


FIG. 2.

FRICTION-TIME CURVE FOR OLEIC ACID TYPE (5% WT OLEIC ACID IN DUO-SOL 65) OF E.P. LUBRICANT.

Type C. Sulphur Type.

This type of curve (Fig. 3) shows no seizure, even at high load, and the frictional torque is uniform throughout the run.

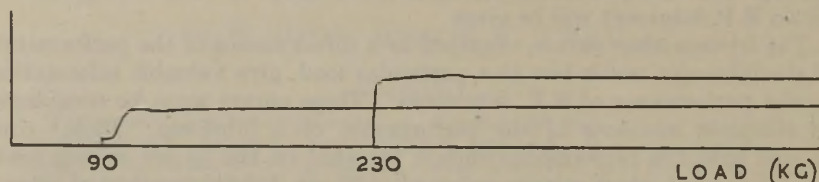


FIG. 3.

FRICITION-TIME CURVE FOR SULPHUR TYPE (0.6% WT SULPHUR IN PENNA 150 NEUTRAL) OF E.P. LUBRICANT.

Type D. Chlorine Type.

This type of curve (Fig. 4) shows rapid or instantaneous seizure, with equally rapid recovery from seizure. The frictional torque is low after seizure and blends showing this type of curve possess, in general, the best E.P. properties. At low loads the curves are somewhat similar to the sulphur curves, but at high loads the characteristic peaks are shown.

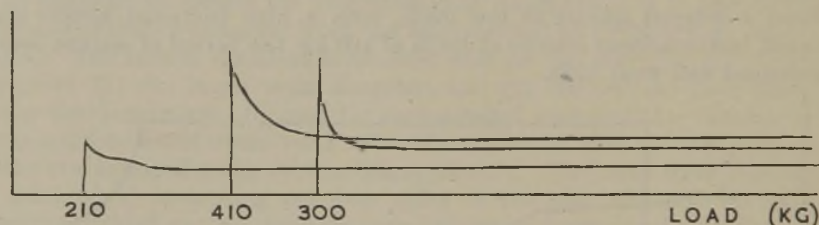


FIG. 4.

FRICITION-TIME CURVE FOR CHLORINE TYPE (NEAT CARBON TETRACHLORIDE -210 AND 410; AND 1% WT $\text{Cl}_3\text{CH}(\text{Oet})_2$ -300) OF E.P. LUBRICANT.

TABLE I.

Compound or blend tested.	Wear-load ratio(s) (kg/mm).	Maximum load (kg).	Friction-time curves.		
			Type of curve.	Seizure.	Frictional torque.
2% Benzyl disulphide + 5% chlorinated paraffin wax.	210.	Tested to 260 kg.	D	Instant >100 kg.	Low-recovery from seizure-good.
Duosol 65.	33.3.	Tested to 102 kg.	A	Rapid >80 kg.	High-seizure prolonged.
0.6% Sulphur.	60 (below 90 kg). 300 (above 90 kg).	Tested to 300 kg.	C	No seizure	Smooth wear-low torque. (See <i>J. Inst. Pet.</i> , 1946, 32, 576.)

New types of friction-time curves, having different fundamental characteristics can be given reference letters, as and when they are discovered.

The results obtained from a series of tests on the four ball machine can thus be given in the form of a table as shown in Table I.

The results given in the Table I are taken from previous papers to illustrate the proposed method of representation of results.

Reference.

- ¹ H. Blok. *J. Soc. aut. Engrs*, 1939, **44**, 193.

ACTON TECHNICAL COLLEGE,
HIGH ST., ACTON, W. 3.

REFERENCE FUELS FOR KNOCK RATING IN SPARK IGNITION ENGINES.

THE octane number scale as proposed by Edgar ¹ has been in general use for about 20 years. The original scale which used 2:2:4-trimethylpentane as the high reference fuel and normal heptane as the low reference fuel has been extended in the upper direction by several methods, two of which are currently in general use. These are:

- (1) The use of *isooctane* with incremental additions of lead tetraethyl as a series of reference fuels;
- (2) The use of blends of heptane and *isooctane* with a constant addition of tetraethyl lead ²: with this scale an arbitrary extrapolation to 120 octane number is used.

The primary reference fuels have not been used in the past in practical testing owing to the prohibitively high cost. Secondary reference fuels consisting of selected straight-run or synthetic gasolines have been laid down and calibrated against the primary fuels on a large number of engines. Although these secondary fuels possess the great advantage of reduced price the following disadvantages are associated with them:

- (1) Not being pure hydrocarbons it is impossible to reproduce any one secondary reference fuel exactly and each batch must be calibrated;
- (2) For the same reason a secondary reference fuel will tend to change in rating if weathered during storage;
- (3) There has been a regrettable tendency to use a different series of secondary fuels for each new test method evolved.

The following fuels have been used in connexion with various knock rating procedures:

<i>Fuel.</i>	<i>Approx. Octane No.</i>
A	40-50
M	20
C	70-80
F	99
S	99

together with certain aviation fuel standards such as the British Air Ministry's BAM 100. In addition some of the above fuels have been used with addition of tetraethyl lead.

To the great relief of all concerned with the knock rating of fuels it is possible now to announce that the primary reference fuels, *normal* heptane and *isooctane*, are now available in such quantities and at such a price that these fuels may be used for all testing procedures.

These fuels have been produced by the Phillips Petroleum Company and the Enjay Company. It is proposed that such primary reference fuels shall be used in all test methods standardized by the Institute of Petroleum and the Standard Methods of Test are being re-written to

designate the use of such fuels. In the meantime, this announcement is made to indicate the decision of the Knock Rating of Aviation Fuels Panel and the Knock Rating of Motor Fuels Panel of the Institute of Petroleum Standardization Committee to specify the use of these fuels forthwith.

Supplies of reference fuels may be obtained from the Petroleum Board and enquiries with regard to such supplies should be addressed to The Secretary, The Institute of Petroleum.

References.

- ¹ G. Edgar. *Industr. Engng Chem*, 1927, **19**, 145.
- ² *J. Inst. Petrol.*, 1941, **27**, 188; 1945, **31**, 418.

THE INSTITUTE OF PETROLEUM HYDROCARBON RESEARCH GROUP.

REVIEW OF PROGRESS, 1945 TO 1947.

In the Institute Notes which appeared in the *Journal* for January, 1945, an article entitled "A New Departure by the Institute" told of the formation of the Research Committee and of the launching of the first research project undertaken by this Committee, namely, the development and application of spectroscopic techniques to problems of hydrocarbon structure and analysis, and associated hydrocarbon synthesis studies.

At that time Dr H. W. Sutherland and Dr G. B. B. M. Thompson, of Cambridge and Oxford Universities respectively, put forward programmes of work in various fields of spectroscopy. Their proposals, which were accepted and sponsored by the Hydrocarbon Research Group, included suggestions for instrumental development work on infra-red and ultra-violet spectrophotometers with particular reference to the application of various electronic techniques developed for other purposes during the war, and the construction of fast direct-reading or recording instruments. A further object of this work was to fill in the gaps in the available data on the infra-red absorption spectra of hydrocarbons, and to use it to develop much-needed correlations between chemical structure and absorption characteristics. At the same time work was sponsored at the Universities of London and Birmingham, under Professor E. E. Turner and Dr W. J. Hickinbottom respectively, on the synthesis of certain pure hydrocarbons in a high state of purity. It has long been recognized, both in Great Britain and the United States, that fundamental and technological problems in the hydrocarbon field depend for their solution on the accumulation of accurate physical data on a large number of reference compounds satisfying very stringent standards of purity. Many of these hydrocarbons may be obtained from the appropriate petroleum fractions by the application of super-fractionation methods, etc., but for others recourse must be had to the slow and exacting methods of chemical synthesis. The U.S. counterparts to the activities of the Hydrocarbon Research Group in this direction are certain Research Projects of the American Petroleum Institute.

During the last 2 years, considerable progress has been made in most of the lines of work covered by the initial programmes, particularly in the spectroscopic field. Perhaps the most spectacular advances have been the developments in spectroscopic instrumentation. These advances have probably set the standard for almost all infra-red spectroscopic work now in progress in Britain, in both academic and industrial research laboratories, as a result of the close contact that has been maintained with instrument manufacturers. The work has undoubtedly been of great value to workers applying these techniques in other fields.

At the present time, the direct-recording double-beam infra-red spectrometer has been developed into a reliable and precise instrument for the determination of infra-red spectra with the minimum expenditure of time

and effort. A further notable advance has been the design and construction of instruments for depicting selected regions of an infra-red absorption spectrum on a large cathode ray oscilloscope in a few seconds. A high-speed technique of this nature opens up exciting prospects of process control and the study of rapidly changing reaction systems, to indicate only two of the many possibilities. Other advances in the field of infra-red methods have included the application of new infra-red detectors and amplifying systems and the study of new materials with the exacting optical properties required for work in this region of the spectrum.

On the ultra-violet side progress has been made in the application of ultra-violet-sensitive photo-electric detectors of the electron-multiplier type to spectrophotometry. This work is of great importance in view of the widespread use of the ultra-violet absorption spectrophotometer in research and analytical laboratories and the parallel development work which is being carried out so vigorously in the United States. In the analysis of hydrocarbon mixtures the value of ultra-violet absorption methods for the detection and estimation of individual aromatic components is widely recognized and fully justifies the substantial support which the Hydrocarbon Research Group is continuing to provide for the exploration of new experimental techniques.

With regard to the compilation and theoretical analysis of spectroscopic data on hydrocarbons, the most important task which is now in progress is the preparation of a detailed record of the large volume of information that had accumulated during the course of intensive wartime researches on the detailed analysis of gasolines and related products. It is anticipated that the complete report will comprise the actual infra-red absorption spectra, a discussion of the known relationships between chemical constitution and specific absorption features, together with criteria of purity and details of the synthesis of the hydrocarbons specially prepared for this work. The report will constitute a record of the substantial contributions made in this field to the British scientific war effort, and will also reveal how several of the investigations now being sponsored by the Hydrocarbon Research Group have arisen. It is hoped to announce in the near future the manner in which this material will appear; a decision on this question has been complicated by paper shortage and the other obstacles to publication which exist at the present time.

The infra-red spectra of several new hydrocarbons of great theoretical interest have been determined and some progress has been made in the theoretical side.

An entirely new field of research has been opened up by the extension of absorption measurements to the centimetric wavelength region by the application of the very high frequency radio techniques developed for radar. This work promises to provide information about molecular properties that would be most difficult to obtain by other methods, and it represents a logical extension of the fundamental research in the infra-red region sponsored by the Hydrocarbon Research Group.

In the field of hydrocarbon synthesis, progress has been somewhat slower, partly as a result of the smaller number of laboratory workers involved and the scarcity of some of the key compounds on which the sequences of preparative work are based.

Some progress, however, has been made in the synthesis of intermediates and some of the hydrocarbons selected in the initial programme have been brought to the stage of final purification and preliminary spectroscopic examination. In the course of this work several novel observations have been made, some of which have been discussed in the scientific Press.

The Group have also been aided in the work at various stages by samples of hydrocarbons which have been prepared under the parallel American Petroleum Institute project. Complete lists of these hydrocarbons have from time to time become available to the Group. Other sources have also contributed high purity products. A complete interchange of reports has also taken place with the A.P.I., so that both sides of the Atlantic have been informed of the other's activities.

A further activity of the Group is the loan of hydrocarbons of high purity to academic research workers. The necessary samples, which would otherwise require the expenditure of much time and money to prepare or purchase, are drawn from a small "bank" of hydrocarbons which was originally set up to serve the wartime researches mentioned above, and which has since been maintained and extended by the Hydrocarbon Synthesis Panel of the Group. Work on the diamagnetic properties, Raman spectra, dielectric characteristics, etc., of hydrocarbons has already been promoted in this way. This aspect of the Group's work is considered to be of the greatest value in interesting University research workers in hydrocarbon problems, and efforts will be made to increase the variety and volume of the "bank's" stocks by contribution or purchase and to extend its operations.

A complete list of the publications which have already appeared, dealing with the work sponsored by the Hydrocarbon Research Group, follows:

- ¹ "Activation of Catalysts in Olefin Reactions", W. J. Hickinbottom. *Nature*, 1946, **157**, 520.
- ² "Instantaneous Presentation of Infra-Red Spectra on a Cathode Ray Screen", E. F. Daly and G. B. B. M. Sutherland. *Nature*, 1946, **157**, 547.
- ³ "Grignard Compounds as Condensing Agents", W. J. Hickinbottom and E. Schlüchterer. *Nature*, 1945, **155**, 19; E. E. Turner and H. J. Shine. *Ibid.*, 1946, **158**, 170.
- ⁴ "Oxidation of Olefins by Peracids", W. J. Hickinbottom and A. Byers. *Nature*, 1946, **158**, 341.
- ⁵ "Infra-red Recording with the Cathode Ray Oscilloscope", H. W. Thompson, *et al.* *Nature*, 1946, **158**, 196, 591; G. B. B. M. Sutherland and E. F. Daly. *Ibid.*, 1946, **158**, 591.
- ⁶ "Use of Lead Sulphide Cells in Infra-red Spectroscopy", G. B. B. M. Sutherland, *et al.* *Nature*, 1946, **158**, 873.
- ⁷ "An Infra-red Spectroscope with Cathode Ray Presentation", E. F. Daly and G. B. B. M. Sutherland. *Proc. phys. Soc. (Lond.)*, 1947, **59**, 77.
- ⁸ "Measurements on the Absorption of Micro-Waves", D. H. Whiffen and H. W. Thompson. *Trans. Faraday Soc.*, 1947, **42** A, 114, 122.
- ⁹ "Some Measurements on the Absorption of Centimetric Waves by Liquid Dielectrics", F. J. Cripwell and G. B. B. M. Sutherland. *Trans. Faraday Soc.*, 1947, **42** A, 149.
- ¹⁰ "Theoretical Interpretation of Vibration Frequencies of Paraffinic Hydrocarbons", G. B. B. M. Sutherland and D. M. Simpson. *J. chem. Phys.*, 1947, **15**, 153.
- ¹¹ "Autoxidation of Olefins: Formation of Unsaturated Alcohols from Olefins by the Action of Organic Peracids", W. J. Hickinbottom. *Nature*, 1947, **159**, 844.
- ¹² "Infra-Red Spectra of C_nD_{2n+2} and the 'Long-Chain Frequency' in Paraffins", N. Sheppard and G. B. B. M. Sutherland. *Nature*, 1947, **159**, 739.

THE INSTITUTE OF PETROLEUM.

SPECIAL GENERAL MEETING.

A Special General Meeting of the Institute of Petroleum was held at Manson House, 26 Portland Place, London, W.1, on July 24, 1947, at 5.30 p.m., to consider and, if thought fit, to pass a Resolution, which was proposed as a Special Resolution, to approve and adopt the revised By-Laws of the Institute dated June 1, 1947.

MR H. C. TETT (Chairman of Council) presided.

THE SECRETARY (Mr F. H. Coe) read the notice convening the meeting.

THE CHAIRMAN : Before we proceed with the formal business, I have to communicate to you an apology from our President, Sir Andrew Agnew. He very much regrets his inability to be with us to-night.

You are all aware of the purpose for which this Special General Meeting has been called, and you are aware of the importance of that purpose. We have been waiting since 1938 for these new By-Laws. A great deal of work has gone into them. You have all had the opportunity to read the very excellent Explanatory Memorandum, which has been sent to all members.

One of the people who has done as much work as anybody, and probably more than anybody else, in connexion with the preparation of these By-Laws is Mr T. Dewhurst. He also is particularly sorry he is unable to be here to-night. He is prevented from being here by an engagement which he feels it impossible to break. He has sent me a letter, which I will read to you :

" I deeply regret my inability to attend the Special General Meeting of the Institute on July 24. As a member of the By-Laws Committee since 1939, and as Chairman of the Committee until February, 1946, I would have welcomed an opportunity of paying a tribute to the very valuable work carried out by Mr Hyams, with the help of the Hon. Secretary, Mr Chilvers.

" The existing By-Laws are inconsistent with the new Articles of Association and are therefore obsolete, whereas the new revised By-Laws are in strict conformity with the Articles, and embody the lessons of more than 30 years experience of conducting the affairs of the Institute. They have been hammered out clause by clause by the By-Laws Committee; scrutinized, checked and approved by the Council; and finally "vetted" and confirmed by the solicitors, who have expert knowledge of these matters.

" In the interests of the Institute, and of all its members, I would express the hope that the revised By-Laws will receive unanimous approval and adoption."

THE CHAIRMAN : I think the views which Mr Dewhurst expresses in this letter are the unanimous views of every member of your Council; a great deal of consideration and careful thought and study has been given by the Council to these new By-Laws.

Although these By-Laws are placed before you as by Council, I think it would be appropriate that the formal resolution proposing their adoption be proposed by the present Chairman of the By-Laws Committee, Mr

Hyams, and seconded by Mr Chilvers, the Hon. Secretary, both of whom have also done a great deal of work in connexion with the By-Laws. I will call on Mr Hyams to move this Special Resolution.

MR H. HYAMS: I think I can say that the Explanatory Memorandum which was circulated to all Corporate members of the Institute gives, with a fair degree of clarity, the reasons for the changes which have been made in the By-Laws, over and above what has been stated in the letter by Mr Dewhurst; and it also details for the information of members, the important alterations that we propose to effect. I think it might be fair, in moving this Resolution, to say very briefly that the directions and the purposes of the amendments and the additions which we submit to you this evening may be summarized under two main headings.

Firstly, as Mr Dewhurst has indicated, it is intended to bring the By-Laws into line with the Memorandum of Association and the Articles of Association, as those documents were amended in 1938, as well as to clarify certain points of detail. This has become necessary because some of the unaltered By-Laws have been found, since 1939, not to be strictly in accordance with the amended Articles of Association. Secondly, we have attempted to give full effect in the new By-Laws to the purpose which the Council had in mind when they proposed, and the members accepted, the change of the name of the Institute, in 1938, from "The Institution of Petroleum Technologists" to "The Institute of Petroleum." The primary purpose of the amendment to the constitution in 1938 was to widen the scope of the membership and to bring within our fold a much more representative section of the petroleum industry than we had been able to encourage into our ranks up to that time. Therefore, we introduced at that stage a "Fellow" grade of member, and we also made it clear that we should welcome the non-technical people, who would come into the "Associate Member" class. But all the time the Council had clearly in mind, and still have clearly in mind, the intention to preserve the professional status of the fully qualified technologist.

So that, in proposing the new By-Laws, one of the primary changes which has been made, has been to clarify the position in regard to the classification of memberships. You will find from the Explanatory Memorandum that the members will fall into two classes—in the technical grades, the "Fellow" category with its junior categories, namely, the "Associate Fellow" and the "Student"; and in the non-technical grades, the "Member" category, with the "Associate Member" and once again the "Student" at the most junior stage.

We do want to make it clear that, whilst we retain the professional status by retaining the "Fellow" and "Associate Fellow," we want to encourage the non-technical people to come within the orbit of the Institute, and we want them to take up full "Membership" or "Associate Membership." For that reason we also make it clear in the By-Laws that in their respective fields the "Fellow" and the "Member" are of equal status, and the "Associate Fellow" and "Associate Member" are also of equal status.

Therefore, in order finally to clarify the situation, we have introduced the "Honorary Fellow" category as a new grade for people of eminence

and of exceptional scientific attainments, whereas before we had the "Honorary Member" only; and we also introduce the "Associate Fellow," the equivalent of the "Associate Member," but requiring that the "Associate Fellow" shall have scientific or technological attainments.

Over and above that we have clarified and regularized the position in regard to Branches. Previously we had no reference at all in the By-Laws as to how Branches were to be formed and how they were to be governed. We have laid down now how a Branch in Great Britain or abroad might be formed, what its governing body is to be, and what may constitute its general membership.

Beyond those comments I do not need to say more, except that I should like to take this opportunity to convey my warmest thanks, as Chairman of the By-Laws Committee, as well as those of my Committee, to my predecessor, Mr Dewhurst, not only for the services which he rendered from 1938 to 1946 as Chairman of the By-Laws Committee, but also for the very wise guidance, and the very useful co-operation which I personally have received from him since I took over the Chairmanship; and to express, too, my appreciation to my colleagues on the By-Laws Committee, with whom, indeed, it has been a great pleasure to work, for the great assistance they have given me in bringing the By-Laws to their present state.

I now desire formally to move this Special Resolution :

"That the revised By-Laws of the Institute dated June 1, 1947, submitted to this Meeting, and a copy of which has for the purpose of identification been subscribed by the Chairman of the Council, be and the same are hereby approved and adopted as the By-Laws of the Institute in substitution for and to the exclusion of the existing By-Laws of the Institute."

MR C. CHILVERS : As Mr Hyams has said, the explanatory memorandum sets out quite clearly the reasons for the changes, and indicates in some detail the more important changes, which have been made in the By-Laws. If you add to that his additional explanation now, and the letter from Mr Dewhurst, which gives something of the background, there is not really very much more for me to say.

There is one point only to which I think reference might be made, that the revised By-Laws take nothing away from the rights and privileges of the Members, Fellows, and Associate Members as they stand at the present time. As Mr Hyams has said, the whole object has been to clarify the position and make the By-Laws more closely in accord with the Articles of Association.

I have much pleasure in seconding the Resolution.

THE CHAIRMAN : Mr Hyams will be glad to answer questions which you may have on these By-Laws. The meeting is now open for discussion.

PROFESSOR J. S. S. BRAME : Will the By-Laws have to be taken *seriatim* or as a whole ?

THE CHAIRMAN : Our solicitor advises us that it is in order to take them as a whole.

MR FRANK DABELL : There is one point on the question of the ballot for election of members of Council. I think the By-Law on that matter reads to the effect that, if the number of names remaining thereon shall exceed the number required, that ballot sheet is cancelled. Is that correct ?

MR HYAMS : Perhaps in fairness to the meeting and the member who raised the question I should read the appropriate extract of the By-Law as proposed in By-Law 73 :

"The Balloting List shall be in such form as the Council may from time to time approve. Each Corporate Member balloting is entitled to erase any name or names from the Balloting List, but any Balloting List shall be deemed invalid if the number of names remaining thereon shall exceed the number required to be elected."

MR DABELL : Some Institutes not only have "if the number shall exceed," but also "if the number shall be less than."

MR HYAMS : I think the intention very clearly is—and it is for the members to say whether they approve—that a ballot paper shall be invalid if the number of names remaining un-deleted from the ballot paper exceeds the number of vacancies that have to be filled. We have always assumed from that, that if, say, there are twelve vacancies on the Council to be filled, and a man desires to vote for only six candidates, so that he deletes the remainder, leaving six un-deleted, the ballot paper is still valid. That is the intention ; it is for the members to decide whether they wish to regard only those papers which have the requisite twelve un-deleted names in the particular instance as being valid papers.

PROFESSOR BRAME : I want to raise one point in relation to the Associate Fellow having "suitable scientific or technological attainments," and "not less than one year's experience in the domain of the science or technology of petroleum." I feel that one year seems a very short time for a man to have had the necessary experience in this industry, even provided he has technological and scientific qualifications.

MR HYAMS : I may possibly find that my colleagues in the By-Laws Committee may want to supplement what I am about to say on this particular question. It was felt that in the case of men who were, in the main, qualified chemists or qualified engineers who had decided to join the petroleum industry, who may possibly have been Student Members of the Institute while they were at college, the fact that they were for twelve months associated in some sort of technical capacity with the industry would qualify them to come out of the Student grade ; and moreover, if a man had been, shall we say, for nine months in a technical post in the oil industry and made his first application to the Institute for membership, it would be, to say the least of it, unwise to elect such a man as a Student. The facts that he has indicated his desire to be associated in some sort of technical capacity with the industry, desires to join the Institute, and has technical training plus one year's experience in some sort of technical post, were considered justification for him to come in to what is after all the lowest technical grade of membership which the Institute has to offer.

MR E. THORNTON : If a man has an Honours " cap," or if in the future, as we hope, there is an examination for which a man has taken perhaps five years of study of petroleum technology, we prefer to say that that man, who has joined the industry, should not wait until he has been in the industry for two years before he can belong to the Institute. It would be undesirable to exclude him from Associate Fellowship.

(The Special Resolution was then put to the meeting, and declared carried unanimously.)

PROFESSOR BRAME : I should like to propose a hearty vote of thanks to the members of the By-Laws Committee, more particularly Mr Dewhurst and Mr Hyams, who have been responsible for the basic work.

MR R. R. TWEED : I have had the opportunity to see and to hear about the enormous amount of work these gentlemen have done, through my attendance at Council meetings, and I am most happy to second the resolution.

(The vote of thanks was accorded with acclamation, and Mr Hyams expressed appreciation on behalf of the Committee.)

The meeting then closed.

OBITUARY.

CECIL EVELYN KEEP.

It is with regret that we record the death at the early age of 48 of Cecil Evelyn Keep.

Gaining his B.Sc. in Oil Mining at Birmingham University in 1921 he entered the employment of Messrs. Steel Brothers & Co. Ltd., and served in India with their oil companies, the Indo-Burma Petroleum Co. Ltd. and the Attock Oil Co. Ltd., until 1934. Most of this period he spent as petroleum technologist with the latter company in the Punjab. In 1925 he obtained his degree of M.Sc.

In 1934 he joined the British Burmah Petroleum Co. Ltd. on their Burma field, where he remained until 1942, rendering noteworthy assistance in the denial of the company's property to the Japanese. From 1942 to 1945 he was in the Calcutta, Johannesburg, and London offices of the company and returned to Calcutta in 1945 as the company's representative in India.

During World War I Cecil Keep served from October 1917 to October 1919 as a Lieutenant in The King's Liverpool Regiment and was in France from July 1918 until October 1919. In the last war he was appointed to the rank of Lieutenant for the period while the denial scheme in the Burma oilfields was in operation, and was "Mentioned in despatches" in recognition of gallant and distinguished services in Burma during the period December 1941 to May 1942.

He first joined the Institute in 1920 as a Student Member and, proceeding through the stages of Associate Member (1924) and Member (1927), was elected a Fellow in 1939. In 1934 he was joint author with H. L. Ward of a paper on "Drilling Against High Rock Pressures with Particular Reference to Operations Conducted in the Khaur Field, Punjab," which was read before a meeting of the Institute. He was also a Fellow of the Geological Society and a Member of the American Institute of Mining and Metallurgical Engineers.

To Mrs. Keep we extend our deepest sympathy.