

## THE INSTITUTE OF PETROLEUM.

A meeting of the Institute of Petroleum was held at Manson House, Portland Place, London, W.1, on Wednesday, January 8, 1947. Lieut.-Colonel S. J. M. Auld, Past-President, was in the Chair.

THE CHAIRMAN, opening the meeting, said : The paper before us to-night is of considerable importance. It is indicative of two things; first, of the way in which petroleum is taking its place in world economy, quite apart from its use as fuels and lubricants; and, secondly, the very great attention we are beginning to realize must be paid to soil and plant pathology if our efforts, at the present time of such importance, are to be successful in making two blades of grass to grow where only one grew before.

MR. LEYLAND COLE presented the following paper, which he illustrated by means of a cinematograph sound film giving a general impression of the process of spraying for plant protection, the damage caused by some of the better known insects and fungi, and tests to indicate the effectiveness of various insecticides.

### PETROLEUM PRODUCTS IN AGRICULTURE: THE RÔLE OF PETROLEUM IN PLANT PROTECTION.

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#### SUMMARY.

The immense loss of food crops, due to weed competition and to the activity of insects and fungi in the field and in the warehouse, is being reduced by the development of new and more effective methods of plant protection.

Petroleum oil has been used for a long time in the form of oil-water emulsions for application to deciduous and to citrus fruit, and in recent years chemicals derived from petroleum have found many applications in agricultural pest control. The base oils of horticultural sprays have certain accepted characteristics, but more work by the biochemist and plant physiologist is required before the perfect spray oil can be evolved. In practice, dilute oil emulsions of various types are sprayed on the tree both in winter and in summer, care being taken to combine maximum insecticidal effect with minimum phytotoxicity. Oil is an excellent insecticide in itself but it is also an important carrier for other insecticides and for fungicides. Certain petroleum fractions possess weed-killing properties and are useful both as selective and non-selective herbicides. Important chemicals derived from petroleum and used in pest control are ester salts, methallyl chloride, and a mixture of dichloropropene and dichloropropane (D-D), the latter being a very successful soil fumigant.



#### INTRODUCTION.

THE disruption and disorganization of war have twice in this twentieth century brought vividly to the forefront the basic importance of food production and distribution and, even in the relatively easy days of peace, when most people take their food supply for granted, more than half man-

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\* Shell Petroleum Company, Ltd.

kind—over 1000 million people—suffer from malnutrition, often to an extent which affects health, reproduction, and life itself. It follows that with increasing world population and with a limited area available for cultivation, it will be necessary in future to devote more attention not only to increasing food production per acre, but also to preventing those losses which are due to weed competition and to the activity of insects and fungi.

The use of petroleum products in agriculture is normally associated with the use of fuel and lubricants in farm machinery, and the extent to which some of these products can assist the farmer in an entirely different fashion is often not realized. It is the purpose of this paper to show how petroleum oil and petroleum chemicals can serve to increase food supplies, by protecting plants and plant products from the natural enemies which so frequently attack them.

The extent to which certain insects and fungi levy a toll upon man's food is seldom realized. Few relatively accurate estimates have ever been made and, in fact, they are extremely difficult to make. It was estimated about 1930 that in the U.S.A. alone the annual loss due to insect pests and fungus diseases amounted to at least £500 million per annum, and the loss due to competition by weeds is probably greater than this.

The concept of a struggle for existence applies to all forms of life. The wild forms of our domestic plants, such as wheat and potato, survived in the struggle in spite of fungal and insect attack because they possessed natural, inherent resistance to fungi and were too widely scattered to be eliminated by their insect enemies. When man selected strains of these wild plants which had, from his point of view, desirable qualities, he frequently reduced natural resistance, and when, at the same time, he massed similar plants together in a wheat or potato field, he produced ideal conditions for the multiplication of insects and fungi, and not infrequently invited a devastating attack. We find, therefore, from very early times records of plant plagues, some of which may have had decisive influence on the history of primitive peoples, leading to their mass migration or, possibly, to their elimination. One may recall Pharaoh's plague of locusts, or the fungal diseases of corn, "blasting and mildew," which according to the Mosaic law would afflict the evildoer.<sup>1</sup>

The history of chemical plant protection goes back to ancient times. Homer, about 1000 B.C., mentioned the "pest-averting sulphur," and Pliny the Elder, A.D. 23-70, records the use of some curious insecticides, one of which was "the gall of a green lizard." Writers in the Middle Ages suggest the use of lime-wash, soap, vinegar, turpentine, sulphur, pepper, soot, and tobacco. Nevertheless, plant protection in the modern sense is a young science, and cannot yet claim more than a few score years of practice.

The organisms which compete with or are parasitic upon food plants are drawn from the whole range of the plant and animal kingdom. In many respects weeds, representative of the higher members of the plant kingdom, are the most persistent and successful of the enemies of man's crops, having a relatively low standard of living, which enables them to grow faster and more profusely than the crop plant, so that the latter is literally overwhelmed and choked to death. As representatives of the lower plants,

the fungi and bacteria are of first importance. Fungi are plants which have no chlorophyll, and must consequently live upon living plants or animals (parasitic fungi) or upon decaying organic matter (saprophytic fungi). Bacteria are now known to cause a number of plant diseases, as well as diseases of man. In the animal kingdom, since all animals are either directly or indirectly dependent on plants for life, they may all be regarded as being parasitic upon the plant, with man, from the plant's point of view, the biggest parasite of any. The plant-parasites in the animal kingdom with which we are concerned, however, are mostly the insects, the mites, and certain plant Nematodes (minute, thread-like worms frequently present in soil).

In waging chemical warfare against the enemies of the plant a variety of methods may be used. Fungi may be controlled by preventing the spores of the fungus from germinating when they alight on the surface of the plant, or in some cases the fungus may be killed on the plant. With insects it is often possible to kill the insect in its egg (using an ovicidal spray), or in its larval stage, as well as in the adult stage. Occasionally it is possible to use a repellent and keep the insect away from the plant to be protected. In all these cases except the last named a notable problem arises which is still imperfectly solved. This is the problem of killing the living fungus or insect while it is actually on the living plant. It will be appreciated that the susceptibility of the crop plant to injury by some chemicals may be greater than or as great as that of the spore or insect to be killed. In this case the chemical is ruled out of use. The spray chemist at all times is compelled to make his product as fungicidal or insecticidal as possible without increasing its phytotoxicity or power to injure the crop plant.

It should be pointed out here that the crops commonly sprayed are orchard fruits, vegetables, and certain tropical crops such as bananas and pineapple, since these are valuable, high-priced crops which can carry the cost of the treatment. As a general rule cereals are not sprayed, but attempts are made to breed varieties resistant to fungi, the chief enemies of grain crops.

#### PETROLEUM OILS AS INSECTICIDES.

The origin of the use of petroleum oils as insecticides is not known, but is probably as old as the knowledge of petroleum itself. Marco Polo in the thirteenth century described the use of crude mineral oil for treating camels against mange, and it is interesting to note that this practice persists to-day in Arabia, except that motor spirit for the purpose is begged from the passing motorist. The relatively modern use of petroleum oils dates from 1865,<sup>2</sup> when kerosine was recommended in the U.S.A. for use on orange trees for the control of scale insects. Undiluted kerosine is capable of burning the tree severely, and crude emulsions were soon devised, soap and milk being used as emulsifiers to enable the kerosine to be diluted with water. Even when diluted, however, the kerosine emulsions often proved to be phytotoxic and, either by intent or by accident, it was discovered about 1905-1910 that lubricating-oil emulsions could be used, the original oils being the partially-refined "red engine oil" type. Following extensive work by Quaintance<sup>3</sup> in 1922, the use of lubricating-oil emulsions, including



the more highly refined white oils, began to spread in the U.S.A., and from about 1925 in the U.K. also.

At the present time many millions of gallons of spray oils are sold. The bulk of the oil is used for application to fruit trees, and knowledge of the properties of horticultural spray oils is based largely on experience with orchard trees, including citrus trees. For this reason, the major part of this paper will deal with orchard sprays, but it is worthy of note that other applications of spray oils in agriculture are developing very quickly.

#### *Base Oils of Horticultural Sprays.*

The physical properties of petroleum oil which are of interest to the spray manufacturer are specific gravity, viscosity, and volatility. The only chemical characteristic used is the figure for unsulphonated residue. At the present time the so-called winter oils, used in the U.K. for application to dormant (*i.e.*, leafless) orchard trees to kill certain insect pests which over-winter on the tree in the egg stage, have a specification as follows :—

Sp. gr.: 0.86 to 0.93 at 15.5°C/15.5°.

Viscosity : 162 to 172 sec Redwood I at 70° F.

Volatility : Not more than 5% distilling at an oil temperature of 350° C.

Unsulphonated residue : Not less than 65% by volume.

On the other hand, the so-called summer white oils, used in temperate climates for application to leaves and fruit in the orchard or glass-house, and in the semi-tropics for application to citrus fruit, have a specification as under :—

Sp. gr. : 0.84 to 0.92 at 15.5° C./15.5° (glass-house oils, 0.84 to 0.89).

Volatility : 10% distilling between 310° C and 340° C

50% distilling between 350° C and 375° C

80% distilling between 380° C and 400° C

Unsulphonated Residue : Not less than 92% by volume (glass-house oils, 95% by volume).

The above statement gives the position in its simplest terms. In practice there is considerable variation, and in California, for instance, the oil used is often selected for the locality in which it will be used, as well as for the time of year and the crop to be sprayed. It should be stated at this stage that the specifications given have been arrived at by a hit-or-miss process, and for the most part are based on field observation rather than on deliberate biochemical research. It is now realized that the physical characteristics of the base oil are quite inadequate as a guide to its biological activity and that far more should be known regarding the chemistry of the oil.

In the preparation of oil-sprays the problem is one of making a suitable oil concentrate which will dilute freely with water, which until recently has been the universal carrier for the oil. In this emulsion concentrate water is the continuous phase, since dilution with water is desired, and oil is the disperse phase, the emulsifier collecting on the oil/water interface. It is, however, possible to use emulsifiers dissolved in the oil, water being absent. The concentrate, which is best described as an emulsible oil, forms an emulsion on being poured into water. The problem of making oil sprays therefore resolves itself usually into one of choosing the appropriate

emulsifiers and method of emulsification, so that a concentrate is produced which is (a) stable in storage for a long time and over a wide range of temperatures; (b) capable of producing on dilution with natural waters of varying hardness and pH a working spray fluid which is itself stable enough to remain unchanged in the spray tank for a number of hours and yet unstable enough to "break" and deposit its oil on the plant surface by impact as well as by drying; (c) capable, when necessary, of carrying an added insecticide or fungicide.

The principal types of oil-spray concentrate are tank mix, stock emulsion, miscible oil, and emulsible oil. The tank-mix method is one of the oldest and, as the name implies, is carried out by stirring oil and water together in the spray tank with suitable quantities of emulsifiers such as soap, if the water is soft, and blood albumen, certain clays, or Bordeaux precipitate if the water is hard. (Bordeaux Mixture is a widely used fungicide made from copper sulphate and hydrated lime.) Tank-mix emulsions are relatively unstable, require vigorous and sustained agitation, can cause grave damage to the tree in unskilled hands, and are not used to any extent in the U.K. Stock emulsions are paste-type emulsions or mayonnaises which contain 70 to 80 per cent of base oil, about 3 per cent of emulsifiers such as casein, and about 20 to 30 per cent of water. The oil-water-emulsifier mixture is passed through an emulsifying mill, care being taken to keep the finished emulsion of a consistency suitable for easy mixing and measuring in the field. Stock emulsions are widely used, especially in hard water areas; they have the disadvantage that they tend to "cream" in storage, and to "break," liberating free oil, if exposed to frost.

The terms miscible, emulsible, and "soluble" are applied to spray concentrates, often somewhat indiscriminately, when these are one-phase solutions which give emulsions when added to a bulk of water. They are all solutions of emulsifiers in oil, the oil eventually forming the disperse phase of the emulsion. It would appear desirable to abandon the use of the term "soluble" in connection with spray oils, and the term "miscible" is employed here to describe spray oil preparations containing a fairly large percentage of emulsifiers (*ca* 15 per cent). The emulsibles, on the other hand, frequently contain 97 to 98 per cent oil, and 3 per cent or less of emulsifier. Miscible oils have been used for many years, the emulsifiers present being, in general, sulphonated fatty acids, resins, or soaps, with a mutual solvent such as cresylic acid and a small amount of water. They mix freely with water if a 50 : 50 slurry is first made before diluting to bulk, and are readily measured and handled. They are not susceptible to frosting, and are easily seen on the tree when sprayed, but they have the serious disadvantage of being incompatible with hard water and with certain insecticide components. Emulsible oils are of fairly recent origin, and are gaining in importance owing to the very much greater range of efficient oil-soluble emulsifiers now available. It seems likely that emulsibles will displace the other types eventually. As examples of emulsifiers used here the proprietary products Emulphor ELA, Triton X-100, Mulsor, and Vatsol may be named, but there are many others.

In use, the oil concentrate is diluted with water so that the spray fluid contains a definite amount of oil. Many experiments have shown that the eggs of over-wintering insect pests on deciduous trees and scale insects on



citrus are controlled by certain percentages of oil, and the dilution rate is adjusted accordingly. In this country a winter-wash for apples will contain about 6 per cent oil as sprayed. Oils for citrus fruit and for application to foliage (e.g., summer orchard sprays, glass-house sprays) are commonly used at 0.75 to 1.5 per cent of actual oil in the ready spray.

### *Insecticidal Action of Petroleum Oils.*

It is unfortunately true that precise knowledge of the mode of action of oils on insect eggs or adults is lacking. The problems of insect physiology which are raised are exceedingly complex. The usual theories are (a) that the oil acts mechanically by coating the egg or entering the trachea of the adult, thus preventing oxygen access or causing carbon dioxide to accumulate, and (b) that the oil acts by direct chemical toxicity on the insect tissues, possibly interfering in some way with enzyme action or actually dissolving fats and causing the disintegration of lipoid tissue.

The first hypothesis—the “stifling” action—would indicate that relatively high-boiling, high-viscosity oils would be the type required and, in general, it is true that the insecticidal and ovicidal properties of winter petroleum oils increase with boiling range or with viscosity until certain minima are reached.<sup>4,5</sup> Martin<sup>6</sup> concluded that the minimum effective viscosity under winter conditions in the U.K. and for oils of more than 60 per cent unsulphonated residue was 125 sec Redwood I at 70° F. The maximum viscosity should be such that ease of handling the oil under winter conditions is retained and 500 sec Redwood I at 70° F is suggested.

It is clear that “stifling” action is not the whole story, since certain insect eggs are unaffected by refined petroleum oils of the type used as base oils for horticultural washes. Thus these oils, which consist mainly of saturated hydrocarbons, cannot kill eggs of apple aphid or apple sucker. On the other hand, tar-oil winter washes, which are rich in aromatic hydrocarbons, give an effective control of aphid and sucker, and this is regarded as a chemical toxic action, being correlated with the content of aromatic hydrocarbons as assessed by solubility in dimethyl sulphate. The winter-washing of fruit trees in the U.K. resolves itself into an attempt to kill the eggs of five major pests, aphid and sucker, controlled by tar-oil and capsid, winter moth and red spider mite, controlled by winter petroleum and not controlled by tar-oil. In order to avoid the necessity for using tar-oil and petroleum washes separately, they are sometimes mixed, but results are often not very good, and the normal, one-spray winter programme in the U.K. commonly employs a DNC-petroleum wash, in which effective control of aphid and sucker is obtained by adding dinitro-ortho-cresol to the petroleum oil.

Many attempts have been made to assess the part played by the unsaturated, sulphonatable compounds in oil, but with conflicting results. Beyond the general conclusion that damage to the plant is largely due to the unsaturates and that oils for application to foliage should not contain more than 4 to 10 per cent sulphonatable compounds, little definite knowledge has emerged. However, recent work by Chapman and Pearce<sup>7</sup> indicates that the origin of the base oil is very important. There is evidence that paraffinic oils are more insecticidal and less phytocidal than naphthenic

types, and that the figure for unsulphonated residue must be interpreted in the light of one's knowledge of the oil type. If this conclusion is generally confirmed it will lead to changes in the current specifications for agricultural base oils and a move in the direction of allowing the chemist and the biochemist, rather than the petroleum physicist, to dictate the specification.

### *Phytocidal Action of Petroleum Oils.*

It has been pointed out earlier that the spray chemist has to solve the problem of killing organisms in contact with the plant without damaging the plant itself. Obviously the problem is easier to solve, in the case of deciduous fruit, when the tree is dormant in winter than when it is carrying sensitive and delicate young foliage, fruit, and shoots. For this reason petroleum oils are applied to deciduous fruit chiefly in the dormant season, or in the "delayed dormant" period preceding bud-burst. In the case of the evergreen citrus tree, oil is applied to foliage and fruit, and experience has shown that the tree is fairly resistant to damage. Highly refined white oil is also applied to deciduous fruit in full leaf, but there is then danger of injury. In all cases trees weakened by malnutrition, drought, or frost are more susceptible to oil injury than healthy, vigorous trees.

Oil injury may be acute, as shown by extensive leaf and fruit drop, or chronic, as shown by bud-kill, delayed bud development, yellowing of leaves, and, in bad cases, death of the wood. Acute injury is often exhibited within a few days of spraying, but chronic injury may take weeks to develop. In the case of oranges, and to a lesser extent grape-fruit, oil injury shows itself as watery patches ("water-spot") on the fruit, especially with navel oranges, and loss of sugars and total solids.

It is now clear that oil penetrates into the plant tissue and causes disturbances in respiration, transpiration, and carbon assimilation; it may also affect the normal production of plant-growth regulators or "hormones" in leaf and fruit. The theory that oil-shock leading to fruit-drop is associated with interference with the production of the "hormone" which prevents the formation of the mature abscission layer in the stalk has received some support recently by field work in which fruit-drop has been prevented by incorporating a synthetic growth regulating substance in a summer white oil-spray.<sup>8</sup>

The penetration of oil into plant-tissue has been studied by de Ong, Knight, and Chamberlin,<sup>9</sup> who found that oils of low viscosity are safer to use on citrus than those of high viscosity. The former oils disappeared from foliage more rapidly than the latter, although this is probably due to absorption rather than to volatilization. It is evident that the quantity of oil retained on the leaf surface is important, as well as the quality of the oil. The oil deposit is affected not only by the oil concentration in the spray applied, but also by the "breaking" qualities of the emulsion. It has been argued, therefore, that for foliage sprays emulsions of the greatest stability consistent with insecticidal efficiency should be used.<sup>10</sup> It is also a well-known rule in practical spraying that trees should never be "double-sprayed" (*i.e.*, sprayed again soon after drying), although this is sometimes difficult to avoid when the spray drifts in a strong wind.

Attempts are now being made to isolate and identify the components in an



oil which are chiefly responsible for the damage. In this work, as in the case of the inquiry into the insecticidal nature of oil, the problems facing the oil chemist and the physiologist are complex. From the grower's point of view it is not sufficient for the spray manufacturer to supply an oil which is generally but not invariably safe in use. In consequence, an oil must be provided which has a wide margin of safety, so that it can be used by spray teams of indifferent skill, on trees insufficiently supplied with nutrients and water, under widely varying climatic conditions, and still without damage to the plant. It is not surprising that perfect spray oils have yet to be evolved.

#### PETROLEUM OIL AS A CARRIER.

In addition to its own inherent properties as an insecticide, either for killing insect eggs on the dormant tree or adult scale insects or mites on leaves and fruit, oil has outstanding properties as a carrier for other insecticides and fungicides. It has been pointed out earlier that a protective cover to leaves and fruit may be necessary, either to prevent the germination of fungal spores which alight on the plant tissue or to kill leaf-eating insects by a stomach poison effect. To take examples, the most important fungus attacking tomatoes in the glass-house is leaf-mould, *Cladosporium fulvum*, which delights in the warm, humid atmosphere provided under glass and can wipe out the entire crop if unchecked. A highly refined white oil, incorporating a fungicide which is a specific for leaf-mould, will give complete control of the fungus, the oil not only killing another common glass-house pest, red spider mite, but also wetting the water-repellent leaf and enabling the fungicide to adhere closely and tenaciously to the leaf and fruit surface. Similarly, a summer white oil can be used with excellent results as a carrier for the contact poison nicotine for the control of woolly aphid (*Eriosoma lanigerum*), which forms the white, waxy filaments so common in summer on neglected garden fruit trees. Here penetration of the nicotine to the aphides protected by their waxy covering would be impossible without the use of oil or other wetting agent.

The importance of oil as a carrier and wetter has been enhanced by the introduction of D.D.T. It is common knowledge that this new insecticide possesses astonishing residual properties as a contact poison. The use of a wettable D.D.T. powder with a petroleum spray is likely to become standard practice for the control of two important orchard pests, capsid bug (*Plesiocoris rugicollis* Fall.) and apple blossom weevil (*Anthonomus pomorum* L/Curt.), for here the residual value of the D.D.T. is given full effect by the "sticking" effect of the oil.

Finally, it seems possible that oil as a combined insecticide and carrier may be even more important in future if atomization procedure becomes standard practice. In this new development water and emulsifiers are discarded, and straight oil, with or without added fungicides and/or insecticides, is "atomized" in a fast-travelling air-stream and carried to all parts of the tree or plant. This process can be adapted both to the orchard and to the field crop, and offers great advantages in speed and cost over the conventional methods. It can also be modified for use in aerial spraying.



## THE PROTECTION OF STORED PRODUCE.

The fight against the insect pests of food and other agricultural products does not cease when the crop is harvested. It is commonly necessary to store cereal grains, peas, beans, and such diverse products as dried fruit, oil seeds, tobacco, cotton, copra, cocoa, and others for considerable periods. Storage may be necessary in an Asiatic "go-down" while awaiting shipment, or in a Canadian grain silo, or in a London dock warehouse. It frequently happens that crops are insect-infested when they come in from the field or plantation, or the storage place itself may harbour many pests. In these cases losses in storage may be very considerable, and more than half the crop may be rendered unfit for use.

In the past the most effective way of dealing with the insect pests of stored produce was to fumigate the material and the warehouse with a poisonous gas, such as hydrogen cyanide, methyl bromide, or ethylene oxide. Fumigation is a skilled job, and is not without danger, owing to the toxicity to men of the gases employed. During recent years attempts have been made to develop safer gases, and one such product on the market is methylal chloride, a highly effective gaseous fumigant derived from isobutylene, itself isolated from cracking gases.

It is now possible also to treat warehouses and silos with a white oil containing pyrethrum or an oil emulsion containing D.D.T. so that a residue toxic to insects is left on the surfaces treated. In this way insects hiding in cracks and crevices can be killed when they emerge, and the treatment of storage places too freely ventilated to be fumigated becomes possible.

## PETROLEUM OILS AS WEED KILLERS.

Weed-killers may be divided into two main classes: those which kill all plants, and those selective weed-killers which kill one plant while leaving another unharmed. Non-selective herbicides are widely used on roads, rail-tracks, and drainage and irrigation ditches. During the past ten years diesel oil has been used on a large scale in citrus groves in California as a non-selective weed-killer. The oil is sprayed over the ground surface at the rate of about 100 gallons per acre, and expensive cultivation and harmful root disturbance are eliminated. After several applications all weeds are destroyed, and a clean surface is left which promotes water retention and permits easy spraying and harvesting operations. It should be noted that this procedure is adapted to flat, irrigated lands. In other areas it might be undesirable to kill all weeds, since serious soil erosion might follow, and here again occasional oiling checks weed growth, while permitting roots to survive and regeneration to occur.

The problem of developing a selective weed-killer is similar to the problem of making an ideal spray oil, for in this case also the object is to kill one living organism while leaving another adjacent organism unhurt. This is by far the most important use of weedicides, and very great advances are likely to be made in this sphere as intensive cultivation spreads and labour becomes more expensive. The most recent contribution to this problem is the introduction of a new range of herbicides—the "hormone" type—which are extraordinarily effective in certain cases. Thus yellow charlock—

one of the worst weeds of English cornlands—can now be eliminated quickly and cheaply by spraying or dusting with 1 lb of 2-4 D (2-, 4-dichlorophenoxy-acetic acid) per acre. This material may also be applied with the fertilizer, so that the corn is encouraged to grow and the weed suppressed in one and the same operation. Some hormone sprays are extremely specialized, and although without effect on grasses and cereals at the dilution used, they are deadly not only to many weeds, but also to the majority of broad-leaved farm crops. Oil is less drastic in its effect, and recently very successful use of kerosine has been reported<sup>11</sup> for the treatment of carrot and parsnip crops. When grown on the large scale these crops absorb much hand labour for weeding, which cannot be carried out mechanically. Kerosines of certain types, sprayed along the rows at the rate of 80 to 100 gallons per acre, can kill most common weeds without affecting the young carrots or parsnips, and cut the cost of weeding to a fraction of its normal figure.

#### PETROLEUM CHEMICALS IN AGRICULTURE.

The chemical industry based upon petroleum which has been developing in mushroom fashion during the last ten years has already produced chemicals of great interest to the farmer. Thus hydrogen obtained from natural or refinery gases is now being converted into ammonia, using atmospheric nitrogen, on a large scale. This ammonia is used as a fertilizer in the form of ammonium sulphate or, by a process developed by the Shell Chemical Co. in California, it may be used in the form of liquid, anhydrous ammonia for injection into irrigation water or into the soil.

During recent years another petroleum chemical which has proved to be of service to the farmer, as well as being of great industrial importance, is the mixture of sodium secondary alkyl sulphates known as "ester salts." This mixture of long-chain alkyl sulphates is made by the reaction of petroleum olefins with sulphuric acid. The acid/olefin reaction mixture is neutralized with caustic soda, and the "ester salts" produced, which are highly surface-active, and fully efficient even in hard water, are used in agriculture as wetters and spreaders for carrying insecticides and fungicides into close contact with insects or foliage. They may also be used with weed-killers and with the plant "hormone" sprays used for the prevention of pre-harvest drop of apples and pears. Mixed with alkalis, they form efficient detergents for removing milk residues from dairy equipment.

One of the most notable of the new additions to the farmer's armoury of chemical weapons is a soil fumigant consisting largely of a mixture of dichloropropene and dichloropropane (D-D Mixture). Hitherto it has been impossible for the farmer to control certain widespread soil pests, and in particular nematodes or eelworms, because although chemical treatments are known, they are insufficiently effective and impossibly expensive. In the glass-house the pests are commonly controlled by steaming the soil, at a cost which may reach £300 per acre. In the field the only remedy, hitherto, has been to avoid growing susceptible crops for a long period of years—a process which may cause considerable monetary loss.

D-D is a dark brown liquid consisting of a mixture of chlorinated C<sub>3</sub> hydrocarbons, of which 1:3-dichloropropene is the most important, produced by the controlled chlorination of propylene and other gases obtained



from certain petroleum fractions. It is injected into the soil by special machines, which place the liquid at a depth of 6 to 8 inches at the rate of 200 to 600 lb per acre. The liquid vaporizes, and the fumigation causes the suppression of a number of harmful soil organisms, including nematodes, wire-worm, and certain fungi, and stimulates the crop, which is sown or planted after fumigation, to more vigorous growth, giving greatly increased yield. A large variety of crops is now being treated with D-D, and extremely good results have been recorded with pineapple in Hawaii and with many market-garden crops in the U.S.A. In the U.K. large areas of some of the most fertile potato and sugar-beet lands are infested with nematodes, and work on the development of D-D for use on the farm and in the glass-house both here and on the Continent is actively in progress.

Time does not permit an account of the way in which petroleum products are being used to combat the three major insect pests—locust, mosquito, and tsetse—which directly or indirectly affect food production, often to a serious extent. It is clear that petroleum is a treasure-house from which the chemist can extract a vast diversity of materials, and from which man can hope to obtain in the future increasing assistance in his unending battle for his daily bread.

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- <sup>11</sup> Hardy, W. D. *Agric. Gaz. New South Wales*, Nov. 1944, LV, part 2.

#### DISCUSSION.

MR. C. L. GILBERT: The lecturer is to be congratulated on having taken us on so interesting and instructive an excursion along one of the more unfamiliar by-paths in the field of petroleum. The subject is comparatively new to most of the members of the Institute of Petroleum, but, nevertheless, it is one of very great importance, out of all proportion to the small quantities of petroleum used as compared with the quantities employed for other purposes. The paper is also of interest as showing how wide are the ramifications of the petroleum industry of the present day, and the extent to which it is necessary for the petroleum technologists to keep in touch with so many other sciences. Indeed, in these days there are very few sciences which are not closely linked with the petroleum industry, and thus it is necessary for the technologist to be a man of many parts. The entomological and biological fields are some distance removed from petroleum technology, so that it is all the more gratifying to find what a major part the petroleum industry is playing in modern developments in this field.

When we try to determine how petroleum products play their part in

practice we are up against the difficulty that we do not know how the composition of oils is related to their behaviour. This suggests that present-day methods of classifying the components of hydrocarbons is quite insufficient. The present classification, in terms of aromatics, paraffins and naphthene hydrocarbons, does not take us far enough. Thus the aromatic class of hydrocarbons occurs in widely different raw materials, and some members of this class may differ from others in their effect on the growths of plant cells, as they do in the case of animal cell growth. Also, in the case of turbine oils and transformer oils, certain members of a particular class of hydrocarbons are technically more significant than others in that class.

The methods described for the protection of plants cover various aspects, including the control of growth of the plant itself. That is a very radical departure, and further research along these lines will probably throw a great deal of light on the life process itself. This technique, therefore, will require very careful control. It seems that if the methods described are fully applied, the resulting increase of crops will be sufficient to provide the world with a really adequate food supply : and it is gratifying that the petroleum industry is taking an active part in this work.

I should like to ask a question which relates to the method mentioned for applying oil in a current of air, rather than in the form of a spray through a nozzle. There is rather a trend in these days to use dusts in the form of very fine particles, or insecticides in the form of aerosols, and it is considered that the finer the particle size, the more effective is the insecticide. I would ask whether, in the case of oil applied by means of an air spray, the intention is to produce small drops which are more effective, or which do less damage to the plants.

MR. LEYLAND COLE : The process of atomizing oil and using air instead of water as the carrier is comparatively new. In regard to particle size one requires, of course, in the case of an ovicidal spray, a certain minimum covering of the egg if it is to be stifled, and perhaps that can be achieved only by using a fair volume of particles of a size considerably above those found in aerosols. Again, in the case of a protective fungicide, a layer of adequate continuity and thickness is required on the leaf and fruit and one must adjust the particle size to give an adequate layer.

However, the technique is new, and we have not progressed far enough to be able to give an answer to your query.

MR. E. G. ELLIS : I should like to express my thanks to the author for his very interesting paper, which I have found so stimulating that I am prompted to ask a number of questions.

The author's mention of sulphur compounds reminds me of an occasion in my early youth, when we prepared a product for the extermination of the Red Spider. We made a most revolting mixture of sulphur and, I believe, potassium oleate ; but it was effective.

My next incursion into this field was to apply a home-made emulsion of mineral oil to rambler roses infested by green *aphis*. I think the *aphis* was slightly resentful, and did not take very much notice ; but the emulsion would have won first prize for phytotoxicity !



An aspect of the subject on which I should have liked a little more information is that of the preservation of produce. Lately we have been hearing quite a lot about the method of preserving fruit and vegetables by coating either with wax, or with mineral oil alone or with a mineral oil emulsion. In this country, so far as I know, the work has been confined mainly to apples, and the method takes the place to a certain extent of controlled gas storage. In other words, the internal atmosphere is so balanced by the diffusion rate of oxygen and carbon dioxide through the layer of wax or oil, that the fruit may be preserved under ordinary barn storage conditions for a considerably longer period than normally.

Work has been done by the Department of Scientific and Industrial Research, and it once more introduced the dual difficulty that, whereas you may have an emulsion which gives apparently, from the physical side, anyhow, a continuous coating, the internal atmosphere is disturbed. For example, the oxygen content will be too low, and although the fruit does not necessarily rot, it may over a period develop what is, to many people, an unpleasant alcoholic taste. I do not find it so unpleasant! At the same time, I understand that the effect on the actual skin of the apple gives rise to difficulty, more particularly with the well-known type of Cox's Orange Pippin, which is particularly susceptible to it, whereas the fruit of the more robust types, such as the Bramley and the Granny Smith, has a natural wax occurring in the skin to a larger extent and is much less susceptible. It has also been found that even the highly refined, acid washed, white oils can themselves be harmful. Far less harmful are vegetable oils of the peanut type; and I believe that a mixture of the two has been used.

The coarser fruit from our own colonies or from America is very much less susceptible, and I understand that it can be kept in an eatable condition by straightforward spray, atomised perhaps, of either the white oils or wax emulsions.

However, perhaps now or later the author may be able to allude further to this very fruitful ground for research.

MR. LEYLAND COLE : I do not think that I can add a great deal to what Mr. Ellis has told us. It is certainly true that arachis oil (peanut oil) has proved more effective than even refined white oils. This work is still proceeding in the laboratories. The great trouble hitherto has been a spotting of the skin of the fruit, leading to internal cell breakdown, for which no one as yet seems to be able to find a remedy.

MR. E. THORNTON : Sometimes it has been found that particular insects can in the course of time adjust themselves to some insecticides of a chemical character, and thereafter continue to breed. Is there any evidence that oil sprays may become less effective in the course of time due to the intended victims adjusting themselves to withstand the attack?

MR. LEYLAND COLE : The answer at the present time is "No." What you have described is true of hydrogen cyanide, particularly when used for fumigating citrus trees, and that is perhaps one of the reasons why oil spraying has succeeded in usurping the position formerly held in some areas

by HCN. It is true also that some insects, particularly those attacking animals, eventually become immune from the effects of arsenic, which is commonly used to control them. But in all these cases arsenic has been used for a long time, and presumably resistant races of insects have been developed. Whether it is possible that oil has not yet been used for a sufficient length of time for that to occur, I do not know, but I rather think the same effect will not be shown. Of course, oil is used largely as an ovicide, or as a carrier for other insecticides and fungicides, with the notable exception that oil alone will control the mites, particularly the Red Spider mite, both the adult and the egg, and also the adult form of many Scale insects.

THE CHAIRMAN : Mr. Leyland Cole has given us, as I expected, an extremely able survey of this field and, as he implied at the beginning, it has needed two dreadful wars to bring this modern civilization of ours to realize what a very narrow margin there is between production and consumption, between a production sufficient to meet the world's requirements, on the one hand, and real danger of starvation on the other hand. But I think we are becoming alert to the situation now, so much so that agricultural specialists are realizing it is not merely a question of the quantity, availability and balance of food nutrients in the soil to which we have to look, but there is something, entirely different and probably of even greater importance in reference to food production, and that is the balance between the plant and its enemies. With the realization of what is required, chemical warfare against such enemies is more and more receiving the attention it deserves.

It is significant that such attention is being paid, not only at the universities and agricultural colleges, but now in the laboratories and experimental stations of our own great oil industry ; and I do not think we need to consider we are praising ourselves unduly in saying that the entry of the petroleum industry into this field is bound to have a very big effect. We are so well furnished in personnel, in knowledge, in technique and in equipment that, if the investigations which are obviously under way progress in the same spirit and to the same extent as other investigations we have made, we are bound to get results which will be reflected in the increased production of food to which the world looks forward.

I would have liked to have been able to discuss the whole of this fine paper, but time does not permit. But I should like to make special reference to the question of soil treatment, with which I am directly personally concerned. Ever since E. J. Russell's work on the so-called partial sterilization of soil it has been quite apparent that the far-reaching effects which were observable would have still wider fields to conquer and that a much more selective application of that method was likely to come. As Mr. Leyland Cole has pointed out, it is not always possible in the ordinary way to go in for what is, after all, the rather crude method of soil steaming to effect this partial sterilization ; it is very expensive and very cumbersome, and even under glass has been largely given up. But the effect of chemicals is quite marked, and in some of my own houses the same soil has been in use for more than twenty-five years, with an annual treatment by chemicals. This is chiefly for tomatoes, which is a crop particularly



susceptible to soil conditions. Such continuous cropping has not by any means reduced the yield; indeed, yields are higher now than at the beginning.

I am very much impressed and encouraged therefore by the author's reference to D-D, emanating so directly from petroleum, and which gives the possibility of this chemical treatment of soil being taken beyond the glass-house to the market garden or even to field agriculture. If he could give us even a broad or a rough idea of what the costs of using D-D are likely to be, as compared with, say, formaldehyde, which has proved very useful against soil fungi, it would be of interest.

The second matter I should like to emphasize is that of weed control. In the case of the carrot crop, for example, we have to consider the specific nature of the selective weed controller. This question of selective control is in its infancy, but close investigation of the various types of growth is quite likely to lead to most effective results. The real and obvious danger, though it is one which can be taken care of, is the upsetting of natural balances, especially in the early stages of growth. But, in view of the encouraging results obtained so far, I think we can look forward to considerable success in selective weed destruction. I can confirm, from my own observations in the United States, the effects of some of the chosen petroleum distillates—mostly by-products of catalytic cracking—on carrot crops and parsnips, which are very difficult to handle and for which hoeing is almost beyond consideration. If the soil is loosened by hoeing, there is the chance, not only of uprooting the carrots, but of letting in fly. If the weed is killed in the early stages, it makes all the difference to the subsequent cropping.

Non-selective weed-killing is much simpler, and here again marked advances have been made in large-scale weed destruction by the use of petroleum distillates, especially where it is wished to get rid of everything that is growing, and just leave the land bare. We started work on this originally because of availability of aromatic products from catalytic cracking. Distillates of boiling range  $350^{\circ}$  to  $650^{\circ}$ , and with an aromatic content of between 60 and 80 per cent. are especially effective. Those with less than 50 per cent. of aromatics tail off markedly in respect of activity; but where this figure is exceeded the cracked petroleum products will destroy annuals with one spraying and, in the case of perennials, two or at most three sprayings are sufficient to clear them away. By this means it has been possible to clear away the greatest weed growths in and around refineries, along railway embankments, and so on. It is important to be able to control such growths because of fire hazards. In the past it has only been possible to do it with arsenates, chlorates, and so on, which are objectionable to animals. The petroleum products are sufficiently volatile so that they will disappear in the course of time.

I look forward with confidence to future developments and to the incursion of the petroleum chemist into this great field of plant protection and the encouraging of cropping by such means.

MR. LEYLAND COLE: I think it will be appreciated that I have dealt with some of these uses of petroleum chemicals in a somewhat sketchy fashion; the danger is that my enthusiasm might run away with me and

I might talk for far too long. That is particularly true of the material D-D, which has great potentialities, and it is also true of weed-killers. The Chairman has asked about the cost of applying D-D, as compared with applying formaldehyde. As you know, formaldehyde is primarily a fungicide and is not capable of killing eelworm, whereas the use of D-D is directed primarily against that pest, as well as against wireworms and other harmful insects. The total cost in the glass-houses will work out, I think, at between £20 and £30 per acre, which is considerably higher than the cost of formaldehyde, but only a fraction of the cost of steaming, and the same sort of figure will apply in the field. The labour cost of hand application is high. We are developing machines for applying D-D in the field and in the nursery and we shall reduce the cost of application in this way.

We do not yet know for how long, under English conditions, the effect of the fumigant will persist. We have good reason to believe that it will last for more than a year, possibly for three years or even longer. Therefore, the total cost must be divided by the number of years over which the effect will persist, in order to arrive at the annual cost. There is an article in *The Scottish Journal of Agriculture* for January, 1947, on independent work with D-D in Scotland, showing that the application of 300 lb of D-D per acre resulted in the three-fold multiplication of a tomato crop; the cost of the application was outweighed many times by the value of the extra crop produced.

With regard to weed-killers, there are many refineries where expenditure on the destruction of weeds on the refinery area is high, since hand labour is used. It is quite clear that some of the materials obtainable at the refinery would to a large extent render that hand labour unnecessary.

It seems that we have a great deal more to learn about petroleum products from the point of view of their use as selective weed-killers, a use which is extremely important and which presents difficult problems. The killing of one growth, whilst leaving another unharmed, is a problem involving the maintenance of a certain margin of safety all the time, because what you can do in experimental work may not necessarily be done by the worker in the field. You may stipulate the application of 50 gallons per acre, but the worker in the field may give a little extra dose "for luck," and so destroy the whole crop. Certainly we do not know enough about the subject yet.

In the case of the non-selective weed-killer, of course, the problem is very much easier. Where one has to clear whole areas, particularly those which are not subject to soil erosion, reasonably cheap oil, if available, does form an admirable substitute for the rather dangerous arsenicals or chlorates which are so widely used.

On the motion of the Chairman, a hearty vote of thanks was accorded Mr. Leyland Cole for his paper.



# THE APPLICATION OF THE PRINCIPLES OF CLAY CHEMISTRY TO PROBLEMS ENCOUNTERED WHEN DRILLING IN TRINIDAD CLAYS.\*

By H. C. H. DARLEY, B.Sc. (ASSOCIATE MEMBER).

## SYNOPSIS.

Such properties of clays as affect drilling problems are discussed. It is shown that with clay-base muds, in order to maintain the characteristics necessary for drilling a high degree of dispersion of the clay particles is required, but that the dispersion agents react on the bit cuttings and formation to cause rapid rises in viscosity, "sticky" drilling with consequent low rates of penetration, and to promote caving. Attempts to mitigate these difficulties with clay-base muds are described. Alternatives to clay-base muds are discussed and the results of laboratory tests of starch muds containing flocculating agents are given. An account is given of the trial of a starch-aluminium sulphate drilling fluid, which gave a marked increase in the rate of penetration but developed excessive gel strengths. The properties of a starch-sodium-chloride-sodium silicate drilling fluid, which appeared to offer a solution to the problems under discussion, are given.

## INTRODUCTION.

Down to the top of the Lower Cruse horizon the formations in Trinidad are mostly sands and sandy clay and generally present no serious obstacles to drilling. Below this horizon the formations are predominantly clays and marly clays. This paper deals solely with problems encountered when drilling in these clays, particularly in the deep wells (below 7000 ft.) where these problems become acute. The difficulties may be summarized as follows :

- (1) High viscosities, due partly to the nature of the formation and partly to the high weights of mud carried (110-150 lb per cu. ft). Because of the high weights muds are very expensive to control;
- (2) Slow rates of penetration. Average rates at 4 ft per hour are quite common and they are sometimes much lower;
- (3) Caving or squeezing formation. This difficulty is not so universal as the first two but is acute in some areas.

These difficulties seldom become great enough to bar further drilling progress, but they render wells tedious and extremely expensive to drill. Since they are due fundamentally to the physico-chemical properties of clays it is along these lines that their solution must be sought.

## RELEVANT CLAY CHEMISTRY.

Before going any further it is necessary to recapitulate briefly such properties of clays as affect these problems.

It is now well established that clays are definite crystalline compounds.

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\* Paper read before Trinidad Branch, Institute of Petroleum, May 1, 1946.

Using X-ray diffraction methods they have been shown to have a layer lattice structure whose units consist of various arrangements of two general types of layers, Si in tetrahedral co-ordination with O and Al in octahedral co-ordination. A clay particle is thus flat, plate-like, and laminar. The particle is surrounded by a layer of bound water and some clays have the power to adsorb water between their units and consequently swell. Clays have the power to adsorb ions—notably cations, principally because of certain substitutions in the lattice, such as tri-valent Al for tetra-valent Si and di-valent Mg for Al, which leave the units with a deficit of positive charge. In general these ions are not rigidly fixed to the surface of the particle, they are free to dissociate and may be exchanged for other ions, this latter property being referred to as base exchange. The various equilibria involved between the undissociated ions on the particle, those in the ion swarm surrounding the particle, and those in the intermicellar liquid are discussed by Davis.<sup>1</sup>

Clays are divided into three main groups, viz :

- (1) The montmorillonite group ;
- (2) The illite group ;
- (3) The kaolinite group.

The montmorillonite group is the most reactive, having a high base exchange capacity and the ability to adsorb water and swell to a remarkable degree. Kaolinite's powers of water absorption and base exchange capacity are very low while the illites vary between these two extremes.

The nature and concentration of ions surrounding the clay particles profoundly influence the properties of the clay. Monovalent ions yield sticky plastic clays, with strong swelling properties. In a suspension the particles disperse to a fine state of division, and the suspension will consequently give low filtration characteristics. Polyvalent ions cause a contraction of the lattice and yield "friable" clays, while in a suspension the particles are flocculated. Excess of monovalent ion also causes flocculation.

There is little available data on the nature of the Trinidad clays dealt with in this paper, but what there is suggests that the main clay minerals are members of the illite groups. In conformity with this, their powers of hydration and swelling are comparatively low. Thus a filter-cake laid down from a clay mud at 100 p.s.i. will contain about 65 per cent water, which may be compared with 90 per cent for a commercial bentonite mud for treating drilling muds.

The Trinidad clays yield sticky plastic pastes and fairly well dispersed suspensions. Drilling muds of good viscosity and filtration characteristics may be obtained at weights of about 75 lb per cu. ft, and it therefore may be deduced that sodium is the dominant ion in these clays.

#### DRILLING PROBLEMS.

The difficulties encountered in drilling may now be considered. In a clay-base drilling mud it is necessary to have a moderately strong concentration of sodium in order to disperse the clay particles sufficiently to give the necessary filtration characteristics. While drilling, chemicals



added to reduce the gel strength and viscosity greatly increase the concentration of sodium. This high concentration of sodium has three objectionable reactions :

(1) It promotes the dispersion of the cuttings into the mud, thereby increasing the rate of viscosity rise. This vicious circle finally results in the liberal addition of water to prevent further rise of shale base (i.e., concentration of clay) with consequent heavy barytes consumption and building up of surplus stocks of mud ;

(2) It will assist in the dispersion of the formation, as it is being cut by the bit, into a sticky plastic mass, thereby seriously retarding the rate of penetration. The importance of this reaction is not generally appreciated and it may therefore be considered further. At rate of, say, 6 ft per hour, the bit takes 10 minutes to cut 1 ft during which time some 100 bbl of mud will have passed at high velocity through the eyes of the bit. This hydraulicking action must result in an intimate mixing of the mud and formation to form a plastic paste. The higher the concentration of clay in the mud, and the higher its concentration of sodium, the more readily will a sticky plastic paste be formed. It is obvious that such a paste will be difficult to drill in the same manner as the farmer finds wet sodium clays difficult to work, and therefore treats them with lime. The worst feature is the readiness with which the bit becomes fouled with clay. The driller wastes much time keeping the bit clean, for once it becomes irrevocably "balled up" further drilling progress is almost impossible.

This is the reason why such relatively soft formations are so slow to drill. It should be noted that the action forms a vicious circle, i.e., the slower the rate of penetration the more time there is for the clays to disperse, and hence the rates vary over wide ranges. Thus, where the formation is fractured or shattered quite high rates are maintained because the formation comes away easily in fragments whose polished surfaces inhibit water entry, and they are quickly carried up the hole before they can be dispersed ;

(3) The sodium in the water filtering into the sides of the hole will increase the tendency for the clays to swell and consequently to cave. As has been stated above the swelling properties of Trinidad clays are not excessive and it is not generally believed that true "heaving shales" occur. Caving is not usually severe, it occurs generally when there is a considerable section of open hole, and it can usually be restrained by increasing the weight of the mud. It is probably primarily due to mechanical instability, and there is evidence that this is sometimes promoted by the lubricating action of the mud penetrating the formation along fracture planes. Nevertheless, any volume change occasioned by the mud filtrates action on the clay will increase the tendency to cave.

#### REMEDIAL MEASURES USING CLAY-BASE MUDS.

From the foregoing it is obviously desirable to reduce the dispersive action of the mud, but the fundamental disadvantage of clay-base drilling

muds is that any measures taken to accomplish this must involve deterioration of their filtration characteristics. Further, it is not practicable to disperse with the use of chemical viscosity breakers. All that can be done is to maintain as low a concentration of clay and of dispersive agents as is consonant with other requirements for the particular conditions of each area.

At the Forest Reserve field some success has been achieved along these lines. Heavy muds are loaded, at a central plant, on special clay bases weighing around 70 lb per cu. ft. The final mud has a water loss of about 15 c.c. in half an hour at 100 p.s.i. Such muds will give about 1000 ft of service before the concentration of clay and chemicals becomes objectionably high. They are then withdrawn and replaced by fresh mud. The installation of a hydraulic classification plant has enabled the barytes to be recovered from old muds. Increased rates of penetration are frequently noted when the mud is changed and the system has the advantage that low viscosities are always maintained at the well without requiring the addition of much barytes.

Again the addition of a flocculating agent to a drilling mud will retard the dispersion of the cuttings and yield less sticky pastes beneath the bit, but with clay-base muds the amount that can be added is severely limited by the sharp deterioration of the filtration characteristics. At the Forest field it was found possible to prepare muds with from 2 to 4 g/litre of  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ . The effect of such small quantities could only be very short-lived, which made the value of the results rather open to question. They did appear, however, to give an increase, sometimes a striking increase in the rate of penetration, and the results were considered sufficiently encouraging to warrant further experiments along these lines. With a clay-base drilling mud, the clay in the mud and the formation clay are essentially similar negative colloids. Therefore to obtain a mud which will not disperse the formation, but be itself dispersed, it is necessary to use some base other than clay.

### SYNTHETIC DRILLING FLUIDS.

Flocculents do not affect the filtration characteristics of organic colloids, such as hydrolysed starch, but the effect of base exchange between the flocculating ions in the filtrate and the formation clays must be considered. A mild concentration of flocculent may be expected merely to counteract the tendency of the clays to swell on contact with water, but a high concentration might cause such a sharp contraction as to initiate caving.

Several synthetic drilling fluids have been described in the literature, viz :

#### (1) Sodium silicate-brine drilling fluids. <sup>2</sup>

This mud prevents disintegration of clay apparently because of the deposition of silica gel which acts as a protective colloid. However these drilling fluids are very expensive and have been found, in Trinidad at least, difficult to handle. Further, the filtration rates are controlled mainly by the viscosity of silicate and hence increase with temperature. Water loss to the formation is distinctly higher than with clay-base muds in good condition.



(2) Positive colloid drilling mud.<sup>3</sup>

The principle of this mud is that conditions which lead to dispersion of positive colloids cause flocculation of negative colloids. It is stated that the mud is somewhat more expensive than silicate-brine muds and its filtration rates are also rather high.

The writer has seen no account of a field trial of this mud.

## (3) Oil-base drilling fluids.

These are generally used to protect low pressure prospective producing horizons from damage from aqueous mud filtrates. An account of a successful oil-base mud is given by A. W. Alexander,<sup>4</sup> but the writer has not sufficient data to consider how far such muds would go towards solving the problems under discussion in this paper.

## LABORATORY EXPERIMENTS AT FOREST RESERVE.

In a search for a suitable synthetic drilling fluid experiments were carried out with hydrolyzed starch, using  $\text{Al}_2(\text{SO}_4)_3$  in various concentrations as a flocculating agent.  $\text{CaCl}_2$  and excess of  $\text{NaCl}$  were also tried. In the case of the first two the starch was hydrolyzed by heating, while in the last, the starch was hydrolyzed with  $\text{NaOH}$  in a saturated solution of  $\text{NaCl}$ .

One of the main objectives was to obtain a mud with an extremely low filtration rate. Therefore no clay at all was used, since clay in the presence of flocculent resulted in the deterioration of the filtration characteristics. The hydrolyzed starch, loaded to 120 lb with barytes, had no absolute gel strength, but the very slow settling rate of the barytes showed that the mud was quite suitable for all practical purposes.

In order to measure the extent to which the flocculents would protect bit cuttings against disintegration, bit cuttings from the Lower Cruse horizon were mixed with the test mud by a high speed electrical stirrer for half an hour, and the proportion of cuttings disintegrated to less than 0.75 m.m. maximum diameter observed. It was noted that the starch contributed to some extent to the protection of the cuttings and that this property deteriorated if the heat of hydrolyzation was not correctly controlled, or if the concentration of  $\text{Al}_2(\text{SO}_4)_3$  exceeded 50 g/litre.

Reasonably representative figures of the effect of the flocculents are given in Table I.

TABLE I.

Mud.	Flocculent.			% of cuttings not dis-integrated.
		g./litre.	m.e.s./c.c.	
Normal clay-base mud	None	—	—	4
3.75% hydrolyzed starch	None	—	—	11
" "	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	30	0.27	37
" "	"	50	0.45	37
3.70% hydrolyzed starch	$\text{CaCl}_2$	30	0.55	40
5%, $\text{NaOH}$ hydrolyzed, starch	Saturated $\text{NaCl}$	—	—	60

A certain proportion of the disintegrated cuttings were dispersed to colloidal dimensions. The greater this dispersion the more the viscosity

and gel strength will increase, though this increase cannot be regarded as a comparative measure of the amount of dispersion permitted by the various flocculents. It was noted that these increases were the greatest with the  $\text{Al}_2(\text{SO}_4)_3$ -muds, which after several runs, had the typical high gel strengths of flocculated clay muds.

In order to gain some idea of the effect of the filtrate on the formation another test was devised. A clay mud, made from Lower Cruse bit cuttings, was given a normal half-hour run at 100 p.s.i. in a wall building tester. The mud was then removed, and the filter-cake left undisturbed in the vessel. The test mud was then introduced and pressure filtered through this clay cake. Since the filtration characteristics of starch muds are virtually unaffected by the addition of flocculents, increases in the rate of filtration could be taken as a measure of the alteration of the clay cake. Although the clay cake could be by no means regarded as identical with the formation clay *in situ*, it was felt this method was more suitable under the particular conditions of the tests, and certainly yielded more statistical results, than the method used elsewhere of immersing formation cuttings in the test mud.

Table II gives some typical results.

TABLE II.

Mud.	Flocculent.			C.c. of filtrate in 16 hrs.	pH of filtrate.	Condition of cake.
		g./litre.	m.e.s./c.c.			
3.75% hydrolyzed starch	None	—	—	22	9.5	No apparent change
"	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	30	0.27	28	9.0	"
"	"	50	0.45	34	6.6	Brittle
3.70% "	$\text{CaCl}_2$	30	0.55	43.5	8.7	"
5% NaOH hydrolyzed starch	Saturated NaCl	—	—	38	8.8	"

Two interesting points in the filtration tests were noted. First, the filtration rate of starch mud through filter paper alone was always greater than through the clay cake and filter paper, typical figures being 2.5 c.c. and 7 c.c. in half an hour respectively. Secondly, with starch- $\text{Al}_2(\text{SO}_4)_3$  muds, the pH of the mud was markedly lower than that of the filtrate. Thus with 30 g/litre of  $\text{Al}_2(\text{SO}_4)_3$  the pH of the mud was 4.2, that of filtrate (filtered through paper) 7.5. This difference diminished with increasing concentration of  $\text{Al}_2(\text{SO}_4)_3$ . Differences in concentration of ions between the residue and filtrate of soil suspensions have long been reported by soil scientists and are often observable in drilling muds. Overstreet<sup>5</sup> discussing theoretical aspects shows that the difference will be the most marked with low concentrations of electrolytes. With these starch muds the effect is beneficial, since it means that less flocculating agent will be carried into the formation. This was clearly shown by comparing the effect of filtering a starch mud containing 30 g/litre of  $\text{Al}_2(\text{SO}_4)_3$  and water containing 5 g/litre of  $\text{Al}_2(\text{SO}_4)_3$  which had the same pH, through clay cakes. With



the starch there was no apparent change in the clay cake, with water it was cracked in pieces.

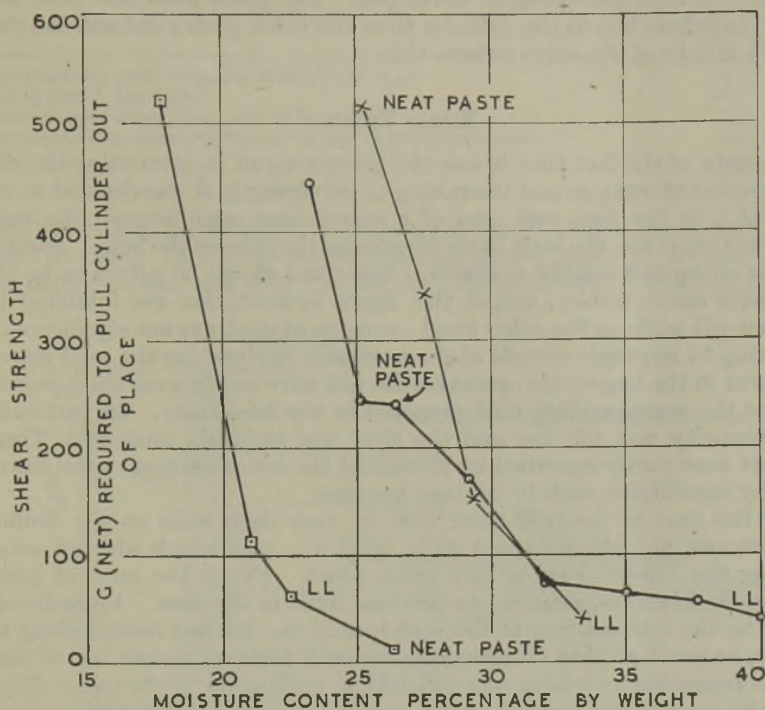


FIG. 1.

PROPERTIES OF CLAY PASTES.

Mud.	Symbol	Weight.	Moisture content, % by weight.		Plastic index.
			Plastic limit.	Liquid limit.	
Normal clay-base mud ex drilling well	×	111	11.3	33.6	22.3
3.75% starch, loaded with barytes, 50 g./litre $Al_2(SO_4)_3$	○	112	12.5	40.0	27.5
5% NaCl saturated, NaOH hydrolysed starch, loaded with barytes	□	112	14.2	22.8	8.6

In the hope of gaining some information of the properties of pastes that would be formed by the various muds with the formation under the bit, test pastes were made up by mixing finely ground bit cuttings with samples of the test muds. Shear strengths at various moisture contents were determined by finding the weight required to extract a hollow brass cylinder immersed in the mud. Plastic limit, liquid limit, and plastic index were also

determined by the standard methods used by soil workers. Results are shown in Fig. 1. The very high liquid limit of  $\text{Al}_2(\text{SO}_4)_3$  treated mud was due to the high gel strengths developed. The paste from this mud was noted to adhere less to the cylinder than the other pastes did and the step in the middle of the curve reflects this.

#### FIELD TRIAL.

In spite of the fact that it was the poorest agent in preventing the disintegration of cuttings and the raising of gel strength, it was decided to use  $\text{Al}_2(\text{SO}_4)_3$  in the first well trial of a starch-base mud because the tests showed that it was the least likely to collapse the sides of the hole. Further it was cheap and readily available. Tests had shown 30 g/litre to be the optimum concentration, and at this figure fermentation was inhibited by the low pH while on the other hand corrosion of steel was not significant.

Owing to improper control of the heat of hydrolyzation the mud manufactured in the large scale operation did not have nearly such good properties as the corresponding mud prepared in the laboratory. In particular the viscosity was too low and the mud was seriously unstable. These defects were partly remedied by increasing the concentration of the starch and by emulsifying with 10 per cent kerosine.

At the time of the trial there were no very deep wells on the drilling programme, and the mud had to be tried in a well which was not penetrating the Lower Cruse to any great depth. Fairly low rates of penetration had been experienced in previous wells in the area. Immediately prior to the introduction of the starch mud the bit had been balling up badly, so much so that on occasions the back pressure caused loss of fluid to the formation and there was difficulty in pulling out of the hole. There was also some loss of water from the mud in the Upper Cruse sands.

When the starch-base mud was introduced there was an immediate and sharp increase in the rate of penetration, and balling up of the bit and the water loss to the formation ceased. The cuttings on the vibrator screen appeared cleaner and harder than with a clay-base mud. No difficulties in handling the mud were experienced, which appeared to fulfil all the necessary functions of a drilling mud satisfactorily. At first the water added to keep the weight from increasing above the required figure was sufficient to keep the viscosity and gel strength normal. However, as drilling proceeded the concentration of  $\text{Al}_2(\text{SO}_4)_3$  fell and the pH rose. Fresh  $\text{Al}_2(\text{SO}_4)_3$  was added but the amount required exceeded what had been anticipated from laboratory results and there were insufficient stocks on hand to maintain the necessary concentration. After drilling 500 ft the pH had risen from 3.8 to 6.4 and the rate of penetration fell off. The gel strength became excessively high and the viscosity began to be affected. The mud was therefore withdrawn and replaced by a normal clay-base mud. At the mud plant it was found possible to recover the barytes from the starch mud, but to do so required a more complicated process than with clay muds.

A comparison of average rates of penetration for 500 ft intervals is given in Table III. In Fig. 2 detailed rates of penetration are plotted against the Schlumberger log. The increase in rate of penetration with the  $\text{Al}_2(\text{SO}_4)_3$



TABLE III.

500 ft Interval.	Rate of penetration, ft/hr.
Immediately prior to using starch-base mud . . . . .	7.9
Using starch-base mud . . . . .	17.8
Immediately after using starch-base mud . . . . .	7.7
Corresponding stratigraphically in well 1400 ft to the W. . . . .	7.0
"          "          "          920 ft to the S.W. . . . .	6.0

mud is striking and the mud may be said to have been successful from this point of view. As regards caving, the results were negative, as caving was not anticipated in this well. While the rate of dispersion of cuttings and

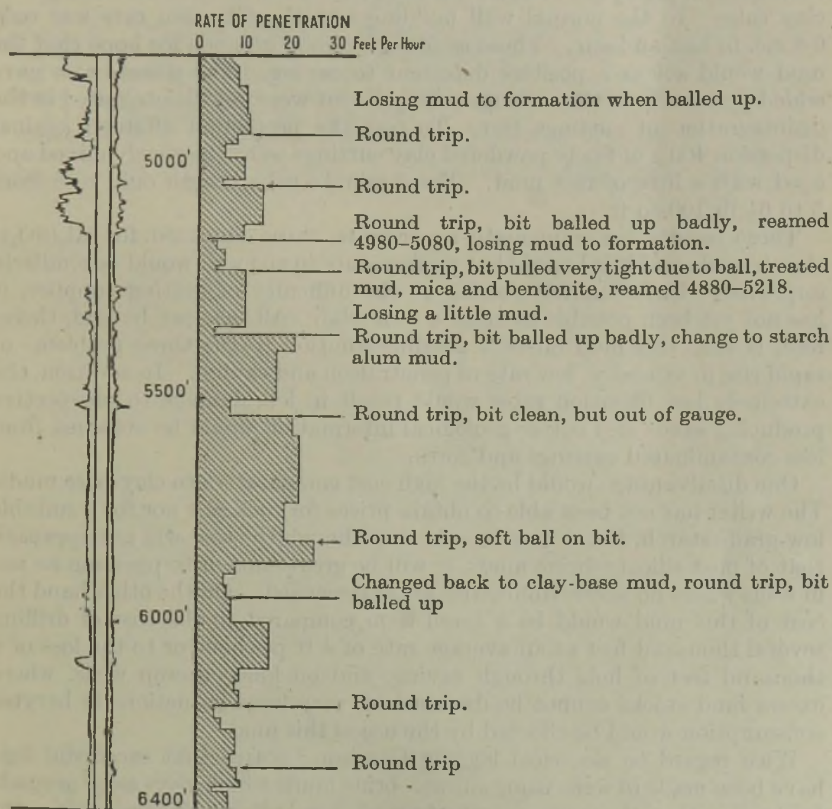


FIG. 2.

INFLUENCE OF DRILLING MUD ON RATE OF PENETRATION.

consequent rise of gel strength was considerably less than with a normal clay-base mud, it was still too high to be tolerated in a flocculating mud, where it could not be reduced by chemical means. Undoubtedly improved

manufacturing technique and the addition of sufficient  $\text{Al}_2(\text{SO}_4)_3$  to maintain the pH around 4 would improve the mud in this respect and enable it to give longer service, but it must be said that laboratory and well results indicate that the development of high gel strength would be a limiting factor to the use of  $\text{Al}_2(\text{SO}_4)_3$  as a flocculating agent.

#### STARCH-BRINE SILICATE DRILLING FLUIDS.

In the laboratory tests described above starch-brine muds gave much the best results in all save the filtration through the clay cake test. Further tests were undertaken to see if this disadvantage could be overcome by the addition of  $\text{Na}_2\text{Si}_2\text{O}_5$ .

The results were most encouraging. The addition of 10 per cent by volume of  $\text{Na}_2\text{Si}_2\text{O}_5$  gave a filtration rate of 21.5 c.c. in 16 hours through the clay cake. In the normal wall building test the filtration rate was only 0.8 c.c. in half an hour. These results give good grounds for hope that the mud would act as a positive deterrent to caving. The silicate also gave added protection to the cuttings. 80 per cent were not disintegrated in the disintegration of cuttings test. To test the protection afforded against dispersion 400 g of finely powdered clay cuttings were vigorously mixed and aged with a litre of test mud. The 5-minute gel strength only rose from 5 to  $6\frac{1}{2}$  lb/100 sq ft.

These results are immensely superior to those obtained for  $\text{Al}_2(\text{SO}_4)_3$  starch muds and it is hoped that performance in the well would be similarly improved. Unfortunately, owing to the difficulty of getting supplies, it has not yet been possible to make a well trial. All that can be said, therefore, is that this mud offers a possible solution to the three problems of rapid rise in viscosity, low rate of penetration and caving. In addition, the extremely low filtration rates would result in less damage to prospective producing sands and better geological information would be obtained from less contaminated cuttings and cores.

One disadvantage would be the high cost comparative to clay-base muds. The writer has not been able to obtain prices for rock salt nor for a suitable low-grade starch, but it may be said that though the cost will not approach that of neat silicate-brine muds, it will be great enough to preclude its use in wells where no severe difficulties are experienced. On the other hand the cost of this mud would be a small item compared to the cost of drilling several thousand feet at an average rate of 4 ft per hour or to the loss of a thousand feet of hole through caving, and on lone outcrop wells, where excess mud stocks cannot be disposed of, very large reductions in barytes consumption would be effected by the use of this mud.

With regard to electrical logging Garrison <sup>2</sup> states that successful logs have been made in wells using silicate-brine muds which gives some grounds for hoping that the same may be true of starch-brine-silicate muds. On the other hand it seems likely that the differences in natural potential would be greatly reduced by using a mud with such a low resistivity. Only field tests can give the final answer and the possibility of having to change back to a clay-base mud when making an electrical survey must be borne in mind.



## CONCLUSIONS.

The work outlined in this paper can only be regarded as a tentative approach to the problem involved. The laboratory work was done in a small routine field laboratory and was therefore rough and far from exhaustive. No conclusions can be reached on the results without extensive field trials. What does seem certain, however, is that a synthetic drilling fluid, of one sort or another, could be evolved which would considerably alleviate the difficulties of drilling deep wells through these clays and give a substantial reduction of the present high drilling costs.

The writer's thanks are due to Messrs. Trinidad Leaseholds Ltd. for permission to publish this paper and to Dr. J. C. Griffiths for criticism and suggestions.

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- <sup>1</sup> Davis, E. "Theories of Base Exchange Equilibriums." *Soil Science*, May 1945.
- <sup>2</sup> Garrison, A. D., and Baker, C. L. "The Chemical Control of Heaving Shale." *Petroleum Engineer*, January 1939.
- <sup>3</sup> Bond, D. C. "Positive Colloid Muds for Drilling through Heaving Shale." A.I.M.M.E. Tech. Pub. No. 1674, 1944.
- <sup>4</sup> Alexander, A. V. "Oil-Base Drilling Muds Often Boost Production." *Oil Wkly*, 4.9.44
- <sup>5</sup> Overstreet, R. "Ionic Reactions in Soils and Clay Suspension." *Soil Science*, April 1945.

# THE CRUDE OIL OF ENGLAND.

By J. S. PARKER, M.A., B.Sc. (Fellow).

## SUMMARY.

The article takes up the history of indigenous crude oil from the field rail sidings of a previous article, which is referenced, and covers its progress through to the finished products.

The period covered is 1942 to 1945 when the main requirements, for war purposes, were lubricating oils and waxes. The stress of the article is thus on the refining of indigenous crude oil for these products.

The quality of the crude oil from the main producing fields for lubricating oil manufacture is first covered. This shows that the crude oils are all of the same general waxy type. Within this general type there are two distinct groups:—

- (1) Paraffin base with low sulphur and asphaltene content and containing lubricating oils of high viscosity index;
- (2) Intermediate base with high sulphur and asphaltene content and containing lubricating oils of medium viscosity index.

Group (1) comprised the major production during the years covered.

Reference is made to similar crudes produced in France and Germany.

The initial laboratory research work on the indigenous crude oil, as guidance for the later practical scale operations, is given in detail.

This is followed by complete detail of all the practical scale operations involved, together with the qualities of the resultant products.

Lastly, general information is given on the total tonnages of the products manufactured and their destination.

In a previous article \* the production of petroleum in England was fully covered. The quality of the crude oil, of primary importance to the refiner, was lightly sketched in and the crude oil flow was traced from the underground oil pool to the rail siding from which it was despatched to the refinery. It is the purpose of the present article to outline the refining qualities of the crude oil from each producing field and to take up the crude oil flow from the previous article and trace its further progress through the refining side to the finished products.

## THE REFINING QUALITIES OF THE CRUDE OIL FROM EACH PRODUCING FIELD.

Regular deliveries of crude oil have been maintained from the three fields—Eakring, Kelham Hills, and Cauntton—and from the small field at Formby. The tonnage delivered was in that order, with Eakring the major producer to Formby with a small but regular production. A full refining outline of the oil produced on each of these fields is set out below.

### LABORATORY FULL-SCALE COMPARISON OF REPRESENTATIVE WELL SAMPLES FROM THE MAIN PRODUCING FIELDS.

#### *Geological References.*

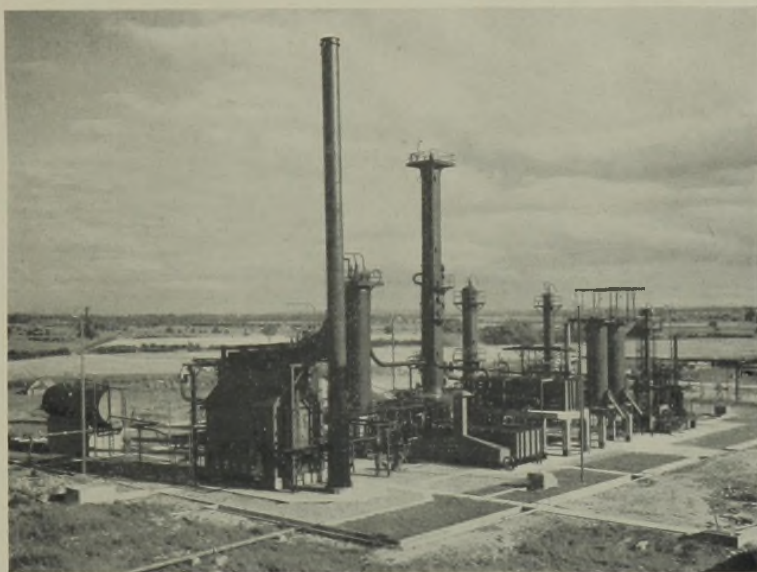
Field.	Reference.	Sand.
Eakring	E.10	Rough rock only.
	E.85	Rough rock, D. Sandstone, Longshaw Grit, and Chatsworth Grit.
Kelham	K.H.32	Upper Grit only.
	K.H.23	Upper and Middle Grits.
Cauntton	C.16	Upper and Middle Grit Groups.
Formby	F.	Taken from road car delivery.

\* Southwell, C. A. P., *J. Inst. Petrol.*, 1945, **31**, 27.



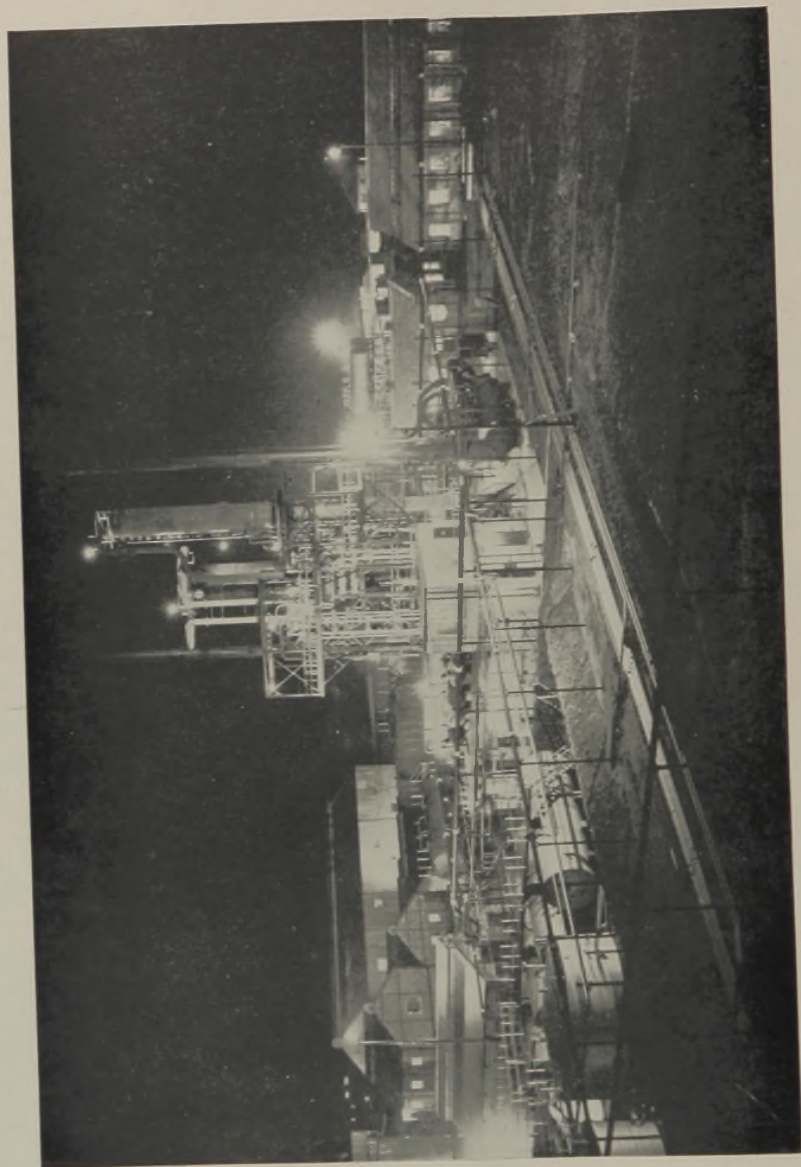


A NEAR MISS AND CONSEQUENT FIRE DID CONSIDERABLE DAMAGE TO  
RAIL SIDINGS.



MODERN U.O.P. CRACKING, POLYMERIZING, AND GASOLINE TREATING  
COMBINED UNIT.

[To face p. 230.]



ALCO DISTILLATION UNIT.



*Analysis of Well Crude Oil.*

	E.10.	E.85.	K.H.32.	K.H.23.	C.16.	F.
Sp. gr. at 60° F	0.851	0.869	0.891	0.889	0.873	0.851
Red. I. Visc. at 70° F, sec.	60 (a)	230	168	190	84	66
Pour point (upper) (I.P. 15/42), ° F	50	10	-40 (b)	-40 (b)	-40	-40 (b)
Wax (U.O.P. A.46/40), %	12.0	8.9	5.2	6.6	9.8	3.7
Asphaltenes (I.P. 6/45), %	Nil	0.05	0.43	0.33	0.44	Nil
Sulphur, %	0.11	0.07	0.53	0.55	0.65	0.14
Acidity, MgKOH/gm	0.05	0.04	0.05	0.05	0.04	0.05

(a) At 100° F. (b) Below -40.

*Distillation (I.P. 24/44).*

	E.10.	E.85.	K.H.32.	K.H.23.	C.16.	F.
I.B.P. ° C	58	60	67	67	58	103
% Vol. at 75° C	1	1	Nil	Nil	1	Nil
" 100° C	3	3	2	1	3	Nil
" 125° C	6	8	3	3	6	4
" 150° C	12	13	6	6	10	10
" 175° C	15	17	8	9	13	14
" 200° C	19	21	12	12	18	19
" 225° C	22	26	15	16	22	25
" 250° C	27	31	20	20	27	30
" 275° C	31	35	26	25	33	37
" 300° C	39	42	35	32	40	46

## DISTILLATION OF WELL CRUDE OIL; PILOT STILL; BATCH OPERATION.

*Typical Distillation Conditions.*

	Cutting temp., ° C.	Cutting press., mm.
Light benzine	145	760
White spirit	190	760
Kerosine	250	760
Gas oil	204	40
Lube A	250	40
" B	275	40
" C	300	40
" D	280	4

*Distillation Product Yields, per cent. by wt on water-free crude.*

	E.10.	E.85.	K.H.32.	K.H.23.	C.16.	F.
Light benzine	12.0	13.7	5.6	5.6	8.1	8.4
White spirit	4.7	4.0	4.2	5.1	6.6	8.0
Kerosine	9.9	10.7	8.6	10.0	11.1	13.4
Gas oil	11.6	10.6	14.1	11.4	12.5	14.4
Lube A	8.8	10.6	11.2	11.4	12.2	13.7
" B	6.8	5.0	7.5	4.6	6.1	4.7
" C	5.6	6.6	10.0	7.6	7.3	7.7
" D	10.7	14.0	5.1	12.0	11.6	7.9
(Total lubes)	(31.9)	(36.2)	(33.8)	(35.6)	(37.2)	(34.0)
Residue	28.0	23.0	31.8	30.5	22.6	20.3
Loss	1.9	1.8	1.9	1.8	1.9	1.5

*Distillation Product Qualities.**Atmospheric Products:*

	E.10.	E.85.	K.H.32.	K.H.23.	C.16.	F.
Light benzine.						
Sp. gr. at 60° F . . . . .	0.742	0.745	0.733	0.724	0.725	0.736
Doctor . . . . .	Pos	Pos	Pos	Pos	Pos	Pos
Octane No. (I.P. 44/46(T)) . . . . .	59	53	51	57	54	63
% vol. at 100° C . . . . .	27	20	30	40	37	19
White Spirit.						
Sp. gr. at 60° F . . . . .	0.792	0.786	0.785	0.784	0.778	0.781
Doctor . . . . .	Pos	Pos	Pos	Pos	Pos	Pos
Kerosine.						
Sp. gr. at 60° F . . . . .	0.818	0.813	0.820	0.825	0.813	0.809
Gas Oil.						
Sp. gr. at 60° F . . . . .	0.840	0.834	0.859	0.861	0.849	0.836
Pour point, ° F . . . . .	5	15	Fld at 0	Fld at 0	5	Fld at 0
Red. I. visc at 70° F, sec . . . . .	41	40	40	42	40	40
Aniline point, ° C . . . . .	74.8	75.8	64.2	65.6	67.9	75.0
Diesel index (I.P. 21/42) . . . . .	62	64	49	49	54	63
Vacuum products.						
<i>Lube A.</i>						
Sp. gr. at 60° F . . . . .	0.851	0.849	0.884	0.884	0.874	0.850
Red. I. visc at 70° F, sec . . . . .	61	63	72	73	67	67
Pour point, ° F . . . . .	55	50	35	35	50	30
<i>Lube B.</i>						
Sp. gr. at 60° F . . . . .	0.856	0.857	0.892	0.893	0.889	0.858
Red. I. visc. at 140° F, sec . . . . .	45	43	49	51	49	48
Pour point, ° F . . . . .	75	80	60	65	70	65
<i>Lube C.</i>						
Sp. gr. at 60° F . . . . .	0.862	0.864	0.904	0.905	0.901	0.864
Red. I. visc at 140° F, sec . . . . .	55	56	67	73	63	53
Pour point, ° F . . . . .	100	100	55	80	85	70
<i>Lube D.</i>						
Sp. gr. at 60° F . . . . .	0.881	0.884	0.925	0.920	0.920	0.878
Red. I. visc. at 140° F, sec . . . . .	84	98	141	133	108	84
Pour point, ° F . . . . .	110	105	90	90	100	75
Residue.						
Sp. gr. at 60° F . . . . .	0.923	0.937	0.975	0.975	0.991	0.956
Red. I. visc at 200° F, sec . . . . .	271	400	950	1420	1450	970
Asphaltenes (I.P. 6/45), % . . . . .	0.6	0.04	3.6	2.4	4.7	1.7
Pour point, ° F . . . . .	50	60	70	70	85	65
Key Fractions (U.S. Bur. Min. R.I. 3279).						
Key Fraction I, ° A.P.I. . . . .	38.6	39.6	35.6	35.2	37.0	39.2
Key Fraction 2, ° A.P.I. . . . .	32.7	32.3	25.0	24.9	25.5	32.3
Class of crude . . . . .	I.P.W.	I.P.W.	I.W.	I.W.	I.W.	I.P.W.

(I, Intermediate; P, Paraffin; W, Wax-bearing.)

## DEWAXING OF LUBRICATING OIL CUTS.

The lubricating oil cuts were dewaxed by the methylene chloride/acetone method using a solvent mixture of 80 per cent by vol methylene chloride and 20 per cent acetone. The temperature of filtration was  $-14^{\circ}$  F. The ratio of solvent oil was 10 to 1 by weight.



	E.10.	E.85.	K.H.32.	K.H.23.	C.16.	F.
<i>Lube A.</i>						
<i>Dewaxed Oil.</i>						
Sp. gr. at 60° F	0.865	0.861	0.892	0.892	0.888	0.855
Refr. index at 60° C	1.4650	1.4620	1.4790	1.4790	1.4790	1.4580
Visc at 100° F, cs	9.22	8.24	9.15	9.01	8.57	8.36
" 210° F, cs	2.35	2.25	2.28	2.29	2.22	2.27
Visc index	70	87	54	63	63	86.5
Pour point, ° F	-5	0	0	0	5	-10
<i>Wax.</i>						
Yield, %	18	18	8	8	13	5
M.p. of wax, ° F (I.P. 76/44(T))	97	97	92	92	97	99
Refr. index of original cut at 60° C	1.4575	1.4555	1.4750	1.4755	1.4715	1.4560
Refr. index of wax at 60° C	1.4300	1.4280	1.4335	1.4350	1.4295	1.4310
<i>Lube B.</i>						
<i>Dewaxed Oil.</i>						
Sp. gr. at 60° F	0.877	0.874	0.903	0.905	0.909	0.866
Refr. index at 60° C	1.4710	1.4700	1.4875	1.4875	1.4915	1.4660
Visc at 100° F, cs	17.2	18.9	22.1	22.9	22.7	17.5
" 210° F, cs	3.47	3.62	3.75	3.84	3.86	3.54
Visc index	77	70	34	35.5	42.5	84
Pour point, ° F	-10	5	-5	5	0	5
<i>Wax.</i>						
Yield, %	27	28	10	10	17.	11
M.p. of wax, ° F (I.P. 76/44(T))	118	118	117	117	115	113
Refr. index of original cut at 60° C	1.4605	1.4610	1.4800	1.4810	1.4785	1.4615
Refr. index of wax at 60° C	1.4325	1.4335	1.4335	1.4355	1.4355	1.4330
<i>Lube C.</i>						
<i>Dewaxed Oil.</i>						
Sp. gr. at 60° F	0.884	0.886	0.916	0.915	0.921	0.874
Refr. index at 60° C	1.4755	1.4755	1.4950	1.4935	1.4980	1.4705
Visc at 100° F, cs	33.4	33.3	50.4	47.1	47.1	24.8
" 210° F, cs	5.14	5.03	5.93	5.75	5.70	4.39
Visc index	86.5	77	50	53	49	90
Pour point, ° F	0	0	0	-10	-5	0
<i>Wax.</i>						
Yield, %	31	30	8	10	16	15
M.p. of wax, ° F (I.P. 76/44(T))	129	125	130	126	125	115
Refr. index of original cut at 60° C	1.4635	1.4645	1.4880	1.4865	1.4870	1.4660
Refr. index of wax at 60° C	1.4360	1.4365	1.4380	1.4385	1.4380	1.4385
<i>Lube D.</i>						
Sp. gr. at 60° F	0.900	0.902	0.930	0.928	0.936	0.889
Refr. index at 60° C	1.4830	1.4835	1.5025	1.5005	1.5085	1.4785
Visc at 100° F, cs	91.9	83.4	148.3	120.0	108.2	57.7
" 210° F, cs	8.84	8.53	10.56	9.44	8.96	7.19
Visc index	69	75	37	41.5	44.5	89.5
Pour point, ° F	-5	-5	-10	-10	-5	0
<i>Wax.</i>						
Yield, %	25	20	7	7	13	16
M.p. of wax, ° F (I.P. 76/44(T))	136	135	138	135	136	114
Refr. index of original cut at 60° C	1.4720	1.4735	1.4980	1.4960	1.4980	1.4730
Refr. index of wax at 60° C	1.4415	1.4420	1.4420	1.4425	1.4460	1.4450

The crude oils are of the same general type and are comparable with analyses already recorded \* for British well crude oil from Hardstoft and Dalkeith, for French crude oil from Pechelbronn, and for the crude oil from certain German fields. They are all wax-bearing with, apart from the volatile fraction, roughly similar product percentages and a high percentage of vacuum residue.

Within this general type the crude oils would appear to range themselves into two distinct groups :—

- (1) Paraffin base with low sulphur and asphaltene content and containing lubricating oils of high viscosity index ;
- (2) Intermediate base with high sulphur and asphaltene content and containing lubricating oils of medium viscosity index.

The (1) group in the above analyses are returned as intermediate paraffin but, with Key Fractions I of 39.6, 38.6 and 39.2 against a paraffin limit of 40, they can be considered, for the purpose in view, as paraffin base.

The well crude oil samples analysed can be classified into :—

Group 1 . . . . .	E.10, E.85, F.
Group 2 . . . . .	K.H.32, K.H.23, C.16.

The refractive indices of the lubricating oil cuts provide additional useful markers for this classification.

In the analyses the Doctor Tests of the light benzines and white spirits are returned as positive. E.10 and E.85 are barely positive, K.H.32, K.H.23 and C.16 are positive. F is very positive owing to a certain proportion of the sulphur content being present in the form of sulphuretted hydrogen.

The refractive indices give a clear indication of the paraffinicity of the dewaxed lubricating oils. F is the most paraffinous, followed closely by E.10 and E.85 and at a lower level by K.H.32, K.H.23, and C.16.

The ideal arrangement for lubricating oil manufacture, if individual tonnages warranted it, would be to segregate and refine separately (a) F, (b) E.10 and E.85 and (c) K.H. 32, K.H.23, and C.16. The quality of the lubricating oils is in that order with Formby giving top quality.

#### CRUDE OIL FLOW.

From the initial attainment of commercial production until the end of 1941 the crude oil was shipped by special train from Eakring to the refinery of the Anglo-Iranian Oil Co., at Grangemouth, Scotland. Here it was subjected to distillation and cracking operations so designed that a maximum percentage of motor spirit and DERV was obtained from the raw material.

Towards the end of 1941 two problems arose for consideration :—

- (1) Transport : The shipment of crude oil by railcar from Eakring to Grangemouth involved traversing the N.E. coast rail bottleneck and

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\* U.S. Bur. Min. Bulletin 401. " Properties of Typical Crude Oils from Fields of the Eastern Hemisphere."



tied up a larger number of railcars on this traffic that would have been necessary on a shorter haul;

(2) Economic : Under the war conditions prevailing lubricating oils and wax, for the manufacture of which the crude was suited, were a more difficult supply proposition than motor spirit or DERV.

The outcome of this consideration was an arrangement by which the Petroleum Board took delivery of the crude oil from the Anglo-Iranian Oil Co., at its Eakring rail sidings and shipped it by rail to Ellesmere Port, Cheshire, where it was refined on behalf of the Petroleum Board, by Lobitos Oilfields Ltd. This arrangement was brought into effect at the beginning of 1942 and has continued to date.

The crude oil was shipped by special train made up to the rail haulage limit of just over 500 tons crude oil contained in about thirty-eight railcars. The railcar complement for this service was roughly the equivalent of three trains. At the production peak 10,100 tons crude oil was shipped per month or one train load every thirty-six hours. The crude oil from the small Formby field was brought in by Scammell road wagons averaging about eleven tons each trip.

The refinery was oriented for the receipt of crude oil by tanker and the despatch of products by road and rail. The receipt of the raw material by rail involved throwing a considerable extra load on the rail sidings. Arrangements were made to unload three sets of six railcars at a time. A few days before this could be checked in operation a near miss and consequent fire did considerable damage to the rail sidings. These were repaired in record time to take two sets of six unloading points and though the third set was eventually put in it was never required except as a reserve. The two sets of six proved to be sufficient.

The railcars were unloaded over the top through the usual swing arm terminated by a 4-in armoured hose. The two 6-in headers were manifolded into the suction of an 8 in  $\times$  8 in  $\times$  10 in duplex D.A. pump alongside the rail siding which pumped through a 6 in line to main storage. Pumping speed was of the order of seventy tons an hour. This speed dropped at low temperature but on no occasion was the crude oil unpumpable from the uncoiled railcars.

The receipts of gross crude oil are shown in Fig. 1, in which the term Eakring is used in its general sense, and includes production from Eakring, Kelham Hills, Cauntton and at isolated periods small lots from Nocton and Hardstoft. The Eakring field was the initial producer, followed by Kelham Hills and later Cauntton and production from the Eakring field at all times dominated the total production. This factor was useful. Segregation of crude oil under the conditions prevailing would have been difficult. The Group 2 crude oil was, however, never present in sufficient percentage to bring the total below its high viscosity index possibilities.

The crude oil was stored in 7,000 or 10,000 ton steam-coiled storage tanks and a stock of 10,000 tons was built up and maintained throughout (a) to act as a reserve against the possibility of transport breakdown, and (b) to reduce the water content from the 2 per cent limit to the 0.5 per cent required for maximum production on the distillation unit.

Prior to the initial switch of the crude oil from Grangemouth to Ellesmere

Port two railcars of average crude oil from Eakring were sent over to check the pumping possibilities of the oil during cold weather. The pour point of the crude oil on a prior sample had been checked at 60° F. It was found that the crude oil had an upper and a lower pour point, the range between the two being of the order of 75° F. The oil remained a pumping proposition from 10° to 20° below its upper pour point.

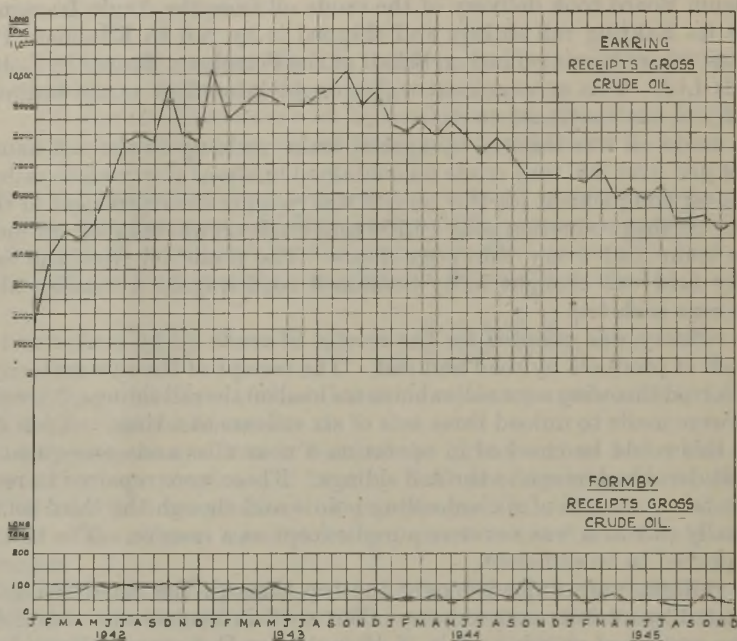


FIG. 1.

The crude oil in these two railcars was sampled in January 1942, and a composite sample of top, middle, and bottom samples was prepared. Research work on a comprehensive scale was carried out on these samples for plant guidance and to obtain information of the product quality possibilities, and extracts from this work are set out below :—

*Research Report on Average Sample of Eakring \* Crude Oil.*

*Analysis of Crude Oil.*

Sp. gr. at 60° F	. . . . .	0.856
Red. I. visc at 70° F, sec	. . . . .	164
Red. I. visc at 100° F, sec	. . . . .	54
Pour point, ° F	. . . . .	60
Wax (U.O.P. A.46/40), %	. . . . .	8.5 (m.p. 124° F)
Asphaltenes (I.P. F.O. 12), %	. . . . .	Nil
Sulphur (I.P. G.O.4), %	. . . . .	0.12
Acidity, MgKOH/gm	. . . . .	0.19
Water (I.P. F.O.14), % by vol	. . . . .	3.9
Salt (as NaCl), %	. . . . .	0.004
Reid vapour pressure, lb	. . . . .	2

\* From the Eakring field. Similar to E.10 and E.85.

*Distillation (I.P. C.P.3).*

I.B.P., °C	58
% vol. at 75° C	1
" 100° C	3
" 125° C	7
" 150° C	11.5
" 175° C	15
" 200° C	19
" 225° C	23
" 250° C	27
" 275° C	32
" 300° C	39

## DISTILLATION OF CRUDE OIL : PILOT STILL : BATCH OPERATION.

A Moore still distillation was carried out to produce a light benzine of end point 150° C, a white spirit of range 150° to 200° C, and a gas oil of range 250° to 300° C. The residue was then distilled under high vacuum to yield 2½ per cent cuts. Twenty-five of these cuts were obtained, leaving a fluid vacuum residue in the still. The vacuum cuts kept their colour well and were waxy at room temperature in the case of those boiling above 375° C at atmospheric pressure.

During the warming up of the still prior to distillation commencing a small amount of uncondensable gas was given off. A certain amount of initial distillation trouble was experienced due to the high water content of the crude oil.

*Yields and Boiling Points of Products.*

Still cut.	% by wt of dry crude.	I.B.P., °C.	F.B.P., °C.	Still pressure, mm Hg abs.	Calculated mid B.P. at 760 mm, °C.
Light benzine	9.7	22	145	—	—
White spirit	7.0	145	195	—	—
Lt. gas oil	17.9	195	290	—	—
Vac. cut 1	1.50	91	120	5	—
" 2	1.60	120	132	4	281
" 3	1.70	132	138	3	300
" 4	1.77	138	143	3	311
" 5	1.73	143	153	2½	322
" 6	1.56	153	164	2½	336
" 7	1.58	164	169	2½	346
" 8	1.43	169	170	2	354
" 9	1.63	170	181	2	365
" 10	1.63	181	188	2	376
" 11	1.50	188	194	2	385
" 12	1.55	194	204	2	395
" 13	1.92	204	207	2	404
" 14	1.56	207	210	2	410
" 15	1.61	210	220	2	417
" 16	1.58	220	227	2	420
" 17	1.72	227	234	2	437
" 18	1.55	234	238	1½	444
" 19	1.63	238	245	1¾	453
" 20	1.55	245	250	1½	464
" 21	1.58	250	256	1½	475
" 22	1.53	256	261	1¾	480
" 23	1.60	261	271	1¾	487
" 24	1.63	271	286	1¾	503
" 25	1.48	286	289	2¾	513
Residue	24.6	—	—	—	—
Loss	1.5	—	—	—	—



A gas oil to meet Pool specification was made up from light gas oil plus vacuum cuts 1 to 9 inclusive. A distillate estimated to be suitable for refining to Pool 5 was made up from vacuum cuts 10 to 21 inclusive. The remainder of the vacuum cuts, 22 to 25, made up a distillate estimated to refine to Pool 12. No cut was viscous enough to refine to Pool 13.

This disposed of all the distillates from the crude oil as follows :—

*Laboratory Result.**Full Scale Result.\**

	% by wt.		% by wt.
Light benzine . . . .	9.7	Light benzine . . . .	9.0
White spirit . . . .	7.0	White spirit . . . .	7.9
Pool gas oil . . . .	31.6	Pool gas oil . . . .	34.4
Pool 5 distillate . . . .	19.4	Pool 5 distillate . . . .	12.0
Pool 12 distillate . . . .	6.2	Pool 11 distillate . . . .	3.7
Vacuum residue . . . .	24.6	Pool 12 distillate . . . .	8.8
Loss . . . .	1.5	Pool 13 distillate . . . .	1.4
		Vacuum residue . . . .	22.7
		Loss . . . .	0.1
	100.0		100.0

\* Average results obtained subsequently on the Alco distillation unit.

*Distillation Product Qualities.**Atmospheric Products.*

	Light benzine.	White spirit.
Sp. gr. at 60° F . . . .	0.7380	0.7946
I.B.P., ° C . . . .	60.5	152.5
F.B.P., ° C . . . .	152	206
% vol at 100° C . . . .	32	—
Aromatics, % by wt . . . .	5.2	13.6
Sulphur, % . . . .	0.01	0.01
Doctor . . . .	pos	Pos
Aniline point, ° C . . . .	52.9	51.7
Critical solution temp, ° C . . . .	52.9	53.1

	Light gas oil.	Pool gas oil.
Sp. gr. at 60° F . . . .	0.8306	0.8427
I.B.P., ° C . . . .	202	213.5
F.B.P., ° C . . . .	335	353
Aniline point, ° C . . . .	67.6	72.5
Sulphur, % . . . .	0.08	0.07
Pour point, ° F . . . .	<0	20
Cloud point, ° F . . . .	<0	22
Diesel index . . . .	60	59
Visc at 100° F, cs . . . .	—	3.60
Flashpoint, ° F . . . .	—	190

*Vacuum Products.*

## Tests on Vacuum Distillates and Vacuum Residue.

Cut no.	Sp. gr. at 60° F.	Visc at 100° F, cs.	Visc at 140° F, cs.	Visc at 210° F, cs.	Red. visc at 140° F, sec.	Cloud point, ° F.	Pour point, ° F.	Refr. index at 60° C.
1	—	3.02	—	—	—	<0°	<0°	1.4619
2	—	4.06	—	—	—	<0°	<0°	1.4588
3	—	5.00	—	—	—	14	10	1.4579
4	—	5.72	—	—	—	24	20	1.4595
5	—	6.74	—	—	—	38	35	1.4610
6	—	8.19	—	—	—	48	45	1.4620
7	—	9.70	—	—	—	56	55	1.4632
8	—	10.36	—	—	—	58	55	1.4654
9	—	11.94	—	—	—	68	65	1.4660
10	0.8645	14.47	7.55	3.27	—	76	70	1.4658
11	0.8663	—	7.91	3.45	45.5	80	75	1.4678
12	0.8684	—	9.12	3.86	49.0	90	85	1.4678
13	0.8700	—	10.77	4.41	54.1	100	90	1.4688
14	0.8720	—	10.32	4.38	52.8	98	85	1.4700
15	0.8728	—	12.33	5.01	59.1	104	95	1.4699
16	0.8764	—	14.98	5.70	67.8	110	100	1.4713
17	0.8802	—	18.08	6.37	78.3	114	105	1.4736
18	0.8839	—	20.84	7.00	87.8	120	105	1.4750
19	0.8854	—	23.18	7.56	96.4	122	105	1.4764
20	0.8877	—	26.14	8.34	107.7	126	110	1.4773
21	0.8892	—	29.43	9.04	120.8	128	110	1.4783
22	0.8913	—	32.57	9.82	134.0	128	110	1.4791
23	0.8923	—	36.53	10.74	149.5	128	110	1.4809
24	0.8941	—	44.88	12.41	182.0	128	115	1.4823
25	0.8976	—	54.66	14.39	222.5	128	115	1.4835
Residue	0.9342	—	—	358 sec. Red. I.	—	—	60	—

*Analyses of Trial Blends of Pool 5 and Pool 12.*

	Pool 5.	Pool 12.
Sp. gr. at 60° F	0.8789	0.8946
Visc at 140° F, cs	15.23	41.3
„ 210° F, cs	5.55	11.53
Red. I. visc at 140° F, sec	68.5	168.5
Pour point, ° F	95	115
Cloud point, ° F	108	130
Wax, %	19	15
Refr. index of blend at 60° C	1.4730	1.4815
„ of wax at 60° C	1.4408	1.4508
„ oil at 60° C	1.4810	1.4878
Melting point of wax, ° F	125	136

In order to obtain a proper index of the response these distillates would show to refining, it was necessary to dewax the distillates before they were solvent refined. This enabled the effect of increasing treatments to be obtained and the treatment losses occurring under these conditions to be determined.

Dewaxing was carried out by chilling the solution of the distillate in dewaxing solvent. The solvent chosen was 30 per cent acetone, 45 per cent benzol and 25 per cent toluol in the ratio of one volume of the distillate to three volume of mixed solvent. The distillates were taken into

solution by warming and the wax precipitated by slowly cooling down to 0° F. The wax was then separated by suction filtration.

*Tests on the Dewaxed Distillates.*

	Pool 5.	Pool 12.
Sp. gr. at 60° F . . . . .	0.8922	0.9022
Visc at 100° F, cs . . . . .	51.51	181.7
"    210° F, cs . . . . .	6.37	13.57
Red. I. visc at 140° F, sec . . . . .	83	225
V.G.C. at 100° F . . . . .	0.838	0.8315
Visc index . . . . .	73	70
Refr. index at 60° C . . . . .	1.4801	1.4869
Pour point, ° F . . . . .	20	15

*Pool 5 Distillate.*

The dewaxed Pool 5 distillate was treated in an Edeleanu pilot plant with a solvent containing 5 per cent benzol and 95 per cent sulphur dioxide. The initial treatment was 200 per cent by vol which was followed by successive 100 per cent treatments up to a point where a viscosity index of 95 to 100 was obtained. Extraction losses were calculated on the amount of extracts obtained and small quantities of raffinate were withdrawn at each stage for later tests.

*Solvent Treatment Results on Pool 5 Dewaxed Distillate.*

Solvent : 5 per cent benzol, 95 per cent SO<sub>2</sub> at 35° C.

Treatment.	Extract, %.	Raffinate.				
		Sp. gr. at 60° F.	Visc at 100° F, cs	Visc at 210° F, cs.	Red. visc at 140° F, sec.	Visc Index.
Dewaxed distillate . . . . .	Nil	0.8922	51.51	6.37	83	73
200% . . . . .	15.6	0.8781	44.32	6.10	79	89
200 + 100% . . . . .	20.8	0.8732	42.29	6.00	77	93
200 + 2 × 100% . . . . .	24.5	0.8701	41.35	5.99	77	96
200 + 3 × 100% . . . . .	27.0	0.8681	40.37	5.95	76	99
200 + 4 × 100% . . . . .	29.4	0.8643	39.55	5.93	75	102

The final raffinate after treatment with 1 per cent floridin at 110° C gave the following results :—

Pour point, ° F . . . . .	25
Cloud point, ° F . . . . .	30
Acidity, MgKOH/gm . . . . .	0.01
Refr. index at 60° C . . . . .	1.4631
Visc gravity constant . . . . .	0.8061
Ramsbottom carbon residue, % . . . . .	0.09
Colour (Lovibond 1 in cell) . . . . .	3.0Y/0.2R
Sulphur, % . . . . .	0.03
Sludging value (I.P.T.O. 21), % . . . . .	0.55

The oil was slightly over-treated as the viscosity index of 95 was reached with the 200 + two 100 per cent treatments and an extract of 24.5 per cent as compared with 29.4 per cent extract for the final treatment. The distillate chosen for Pool 5 has proved heavy for the 55 to 75 sec. Red. I



viscosity specification. A 10 per cent lower distillate viscosity could be set in practice.

Two waxes were removed in the dewaxing process, a considerable quantity of a hard oil-free wax and a small quantity of low melting-point wax not quite free of oil.

*Characteristics of the Waxes from Pool 5 Distillate.*

	High melting-point wax.	Low melting-point wax.
Setting point, ° F	132.2	118.1
Refractive index at 60° C	1.4390	1.4389
Yield % of distillate by wt	15.0	0.8

The high melting-point wax was dry and hard but not crystalline in appearance. Its colour was very good. The low melting-point wax was crystalline in character and also had a very good colour. Both waxes blended would have a setting point of 131.5° F and a yield of 15.8 per cent by weight on the distillate.

*Pool 12 Distillate.*

The dewaxing filtration was more rapid and complete than that on Pool 5 distillate and the pour point was 5° F lower despite the high viscosity of the Pool 12 distillate. As it was considered that a heavier solvent treatment would be required for this Pool 12 dewaxed distillate, the solvent ratio was changed to 10 per cent benzol, 90 per cent sulphur dioxide.

*Solvent Treatment Results on Pool 12 Dewaxed Distillate.*

Treatment.	Extract, %.	Raffinate.				
		Sp. gr. at 60° F.	Visc at 100° F, cs.	Visc at 210° F, cs.	Red. visc at 140° F, secs.	Visc index.
Dewaxed distillate	Nil	0.9022	181.7	13.57	225	70
300%	13.9	0.8879	137.5	12.27	185	85
300 + 150%	17.3	0.8832	127.4	11.90	177	88
300 + 2 × 150%	20.3	0.8808	122.3	11.61	172	89
300 + 3 × 150%	22.5	0.8784	116.6	11.43	165	91

The final raffinate after treatment with 1 per cent floridin at 110° C gave the following results :—

Pour point, ° F	25
Cloud point, ° F	26
Acidity, MgKOH/gm	0.01
Refr. index at 60° C	1.4699
Visc gravity constant	0.8056
Ramsbottom carbon residue, %	0.10
Celour (Lovibond $\frac{1}{2}$ in cell)	9.7Y/1.6R.
" " 1 in cell)	20.0Y/3.4R.
Sulphur (total), %	0.08

*D.T.D. 472 Oxidation Test.*

Coke before oxidation, %	. . . . .	0.10
Coke after oxidation, %	. . . . .	0.71
Rise in coke value, %	. . . . .	0.61
Visc ratio	. . . . .	1.44

The final raffinate is slightly under-refined as the viscosity index is only 91+. The sulphur content of the finished oil is quite low (0.08 per cent) in view of the heaviest distillates made being present in this blend and the fact that the residue has a sulphur content of 0.24 per cent.

Only one wax was obtained from this blend and it was a hard light yellow wax of amorphous appearance.

*Characteristics of the Wax from Pool 12 Distillate.*

Setting point, ° F	. . . . .	146.0
Refr. index at 60° C	. . . . .	1.4439
Yield, % by wt of distillate	. . . . .	11.0

## SAMPLE FROM FULL SCALE PRODUCTION.

A sample of Pool 13 distillate was taken from distillation unit production.

The sample was first dewaxed by the method used for Pool 12 distillate. The wax was de-oiled in solution in solvent and had a firm but not hard structure. It was brown in colour and amorphous in appearance. The filtration of the chilled dewaxing mixture was very slow, the wax being greatly swelled up by the solvent.

The solvent used for solvent treatment was 15 per cent benzol, 85 per cent sulphur dioxide. Samples of raffinate and extract were taken throughout the process.

*Pool 13 Distillate.*

Sp. gr. at 60° F	. . . . .	0.9045
Visc at 140° F, cs	. . . . .	74.82
„ 210° F, cs	. . . . .	17.90
Red. I. visc at 140° F, sec	. . . . .	304
Pour point, ° F	. . . . .	115
Wax content, %	. . . . .	15.0
Refr. index at 60° C	. . . . .	1.4871
„ of wax at 60° C	. . . . .	1.4521
„ of oil at 60° C	. . . . .	1.4924
Melting point of wax (bulb), ° F	. . . . .	141

*Pool 13 Dewaxed Distillate.*

Visc. at 100° F, cs	. . . . .	381.0
„ 210° F, cs	. . . . .	21.33
Visc Red. I. at 100° F, sec	. . . . .	1539
„ 140° F, sec	. . . . .	420
„ 210° F, sec	. . . . .	89.5
Pour point, ° F	. . . . .	20
Visc index	. . . . .	69
Refr. index at 60° C	. . . . .	1.4915
Visc gravity constant	. . . . .	0.8331

*Solvent Treatment Results on Pool 13 Dewaxed Distillate.*

Treatment.	Extract. %.	Raffinate.				
		Sp. gr. at 60° F.	Visc at 100° F, cs.	Visc at 210° F, cs.	Red. visc at 140° F, sec.	Visc index.
Dewaxed distillate .	Nil	0.9114	381.0	21.33	420	69
300% .	17.3	0.8956	268.7	18.51	320	82
3000 + 100% .	21.5	0.8924	245.8	17.83	305	84
300 + 2 × 100% .	24.4	0.8905	233.5	17.48	290	87
300 + 3 × 100% .	26.9	0.8886	223.7	17.21	280	89
300 + 4 × 100% .	28.9	0.8860	217.3	16.95	275	89
300 + 5 × 100% .	31.2	0.8844	209.8	16.73	275	91

The final raffinate after treatment with 2 per cent floridin at 110° C gave the following results :—

Pour point, ° F .	25
Acidity, MgKOH/gm .	0.01
Refr. index at 60° C .	1.4701
Visc gravity constant .	0.8039
Ramsbottom carbon residue, % .	0.19
Colour (Lovibond), $\frac{1}{8}$ in cell .	7.5Y/0.9R
$\frac{1}{4}$ in cell .	20.0Y/2.3R
Sulphur total, % .	0.09
Cloud point, ° F .	28

*D.T.D. 472 Oxidation Test.*

Coke before oxidation, % .	0.19
Coke after oxidation, % .	0.52
Rise in coke value, % .	0.33
Visc ratio .	1.14

*Characteristics of the Wax from Pool 13 Distillate.*

Setting point (I.P.T.), ° F .	144.7
Refr. index at 65° C. .	1.4521
Yield, % of distillate .	15.3

## FULL SCALE OPERATION.

*Distillation.*

The indigenous crude oil was distilled on an Alco distillation unit \* into three atmospheric products, one vacuum overhead, four vacuum side-streams and a vacuum residue. The product cuts remained standard at light benzine, white spirit, gas oil, light spindle, heavy spindle, light lube, heavy lube, cylinder stock, and vacuum residue.

The light spindle contained only a wax trace and was, to a large extent, cut back into the gas oil. The front end of the wax showed up in the heavy spindle.

The average product percentages have already been given (p. 238), where Pool 5 is heavy spindle, Pool 11 light lube, Pool 12 heavy lube, and Pool 13 cylinder stock.

\* *Petrol. Times*, 1934, 32, 435; *Refiner*, 1935, 14, 140.



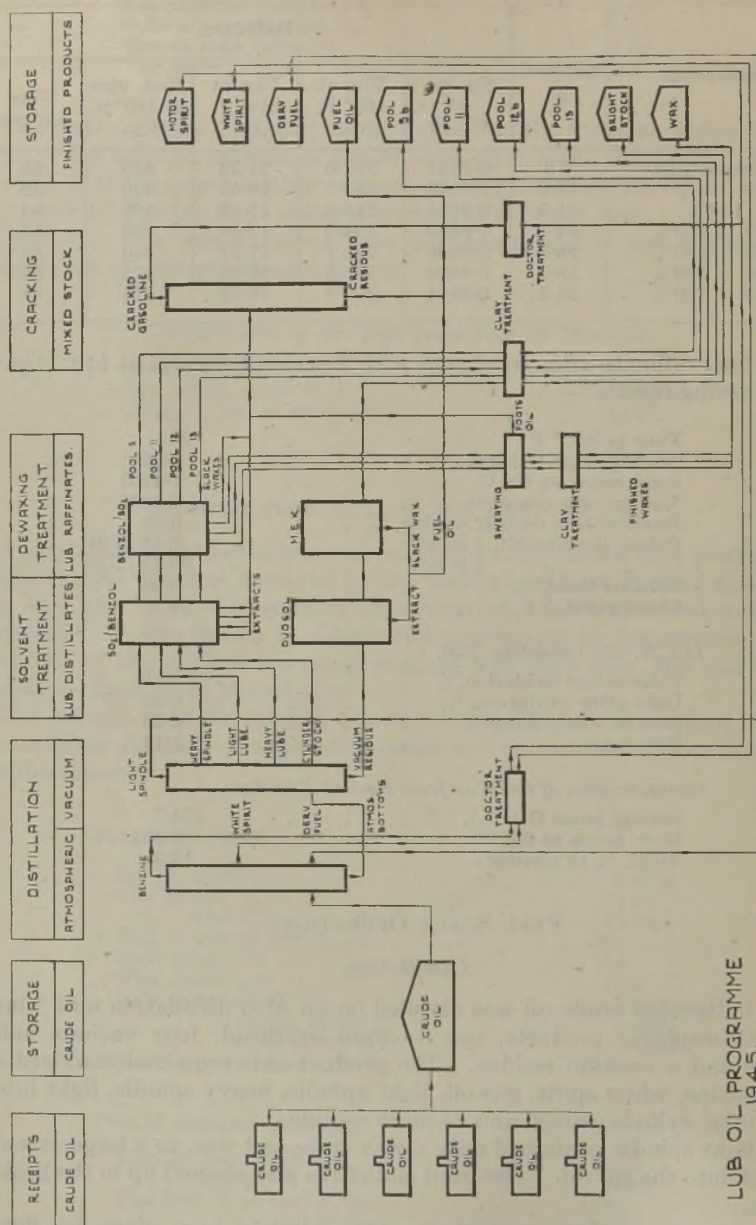


FIG. 2.

FLOW SHEET—INDIGENOUS CRUDE OIL.

Full rated throughput was easily maintained on this crude. The only abnormal feature was the vicious HCl corrosion of tube bundles compared with the small salt content of the crude. It was necessary to inject ammonia into the vapour lines.

### *Motor Spirit.*

The light benzine was given a doctor treatment and was blended back with indigenous cracked gasoline to obtain front end volatility and an octane number around 70. The blend was made up in accordance with the ruling Service requirement. Typical examples of the two components and a finished blend are given below :—

	S.R. benzine.	Cracked gasoline.	Blended motor spirit.
Sp. gr. at 60° F . . . . .	0.724	0.729	0.726
Colour . . . . .	W. white	W. white	W. white
Doctor . . . . .	Negative	Negative	Negative
<i>I.P. Distillation :</i>			
I.B.P., ° C . . . . .	36	33	33
% vol at 63° C . . . . .	8	17	10
" 100° C . . . . .	47	38	46
" 115.5° C . . . . .	81	56	62
" 140° C . . . . .	96	76	84
F.B.P., ° C . . . . .	144	179	174
Reid vapour pressure, lb . . . . .	8.0	10.5	9.7
Total sulphur, % . . . . .	—	0.07	0.02
Corrosive sulphur (A.S.T.M.) . . . . .	—	Nil	Nil
Gum, existent, mg/100 ml . . . . .	—	1	1
Octane No., (A.S.T.M.) clear . . . . .	64	74	71
" 1 ml TEL/Imp. gall. . . . .	—	78.5	78
" 2 ml " . . . . .	—	80.2	81
" 3 ml " . . . . .	—	80.8	82.4

### *White Spirit.*

The White Spirit was given a doctor treatment and was marketed in accordance with the ruling Pool specification for this grade. The following is a typical analysis :—

Sp. gr. at 60° F . . . . .	0.790
Colour . . . . .	W. white
Flashpoint (Abel), ° F . . . . .	91
Corrosive sulphur . . . . .	Pass
Average sulphur after doctor treat, % . . . . .	0.03

### *I.P. Distillation :*

I.B.P., ° C . . . . .	144
F.B.P., ° C . . . . .	197

### *Gas Oil.*

The gas oil was marketed straight or blended with a minor percentage of light spindle distillate. The main usage was as DERV fuel. A typical example of the latter is :—

Sp. gr. at 60° F . . . . .	0.850
Colour (Lovibond 1 in cell) . . . . .	2.0Y/0.2R
Flashpoint (P.M. closed), ° F . . . . .	184
Red. I. visc. at 70° F, sec . . . . .	42
Pour point, ° F . . . . .	25
Cloud point, ° F . . . . .	32
Acidity, MgKOH/gm . . . . .	0.03
Aniline point, ° C . . . . .	74.1
Diesel index . . . . .	58

*I.P. Distillation :*

I.B.P., ° C . . . . .	206
F.B.P., ° C . . . . .	374

*Lubricating Oil Distillates.*

These were refined and dewaxed in an Edeleanu combination solvent treating and solvent dewaxing unit.

*Vacuum Residue.*

This was initially cracked, but for the major part of the war period it was pumped over to "Shell" Refining and Marketing Co. Ltd. for Duosol treatment followed by MEK dewaxing.

## SOLVENT TREATMENT AND SOLVENT DEWAXING.

*Edeleanu SO<sub>2</sub>/Benzol Treating and Dewaxing Unit.*

The waxy lubricating oil distillates were solvent treated and solvent dewaxed on a combination SO<sub>2</sub>/benzol unit designed for this purpose. These units were developed to practical scale just prior to the war and have not yet been fully described in the literature.

The principle consists of the multiple stage treatment of the distillate with a solvent comprised of, say, 90 per cent SO<sub>2</sub> and 10 per cent benzol. The raffinate from this treatment, after removal of the solvent, is carried forward and mixed with solvent comprised of 10 per cent SO<sub>2</sub> and 90 per cent benzol. This mixture is chilled, utilizing SO<sub>2</sub> for the refrigeration, and passed through rotary filters where the wax content is removed.

The resulting products from the combined operation were filtrate, slack wax, and extracts. The solvents were recovered by evaporation and compression and re-used.

This unit, though not far advanced from pilot plant stage, operated satisfactorily throughout the war at full rated throughput.

*Pool 5 Distillate.*

Finished grade . . . . .	Pool 5L.
Solvent treatment . . . . .	100% of 90% SO <sub>2</sub> /10% benzol. 3 stage at 20/35° C.
Solvent dewaxing <sup>a</sup> . . . . .	Dilution 1.4/1. Solvent 15% SO <sub>2</sub> /85% benzol (by wt).
Filtrate yield . . . . .	65.7% by wt.
Extract yield . . . . .	17.8% by wt.
Slack wax yield . . . . .	16.5% by wt.



	Distillate.	Filtrate.	Extract.	Slack wax.
Sp. gr. at 60° F	0.882	0.870	0.997	0.813
Flashpoint (P.M. closed), ° F	420	410	405	405
Red. I. visc at 140° F, sec	63	60	165	—
Pour point, ° F	85	25	20	—
Acidity, MgKOH/gm	0.04	—	—	—
Wax content, % by wt	17	—	—	—
Colour (A.S.T.M.)	—	1½	—	—
Visc (Kin) at 100° F, cs	—	29.4	—	—
" at 210° F, cs	—	4.81	—	—
Visc index	—	88	—	—

Melting point of slack wax, ° F	127
" pure wax, ° F	129
Refr. index at 60° C of slack wax	1.4380
" pure wax	1.4370
" oil	1.4670
Oil content of slack wax, %	8

Finished grade	5b.
Solvent treatment	200% of 90% SO <sub>2</sub> /10% benzol. 3 stage at 30/40° C.
Solvent dewaxing	Dilution 1.9/1. Solvent 10% SO <sub>2</sub> /90% benzol (by wt.).
Filtrate yield	62.6% by wt.
Extract yield	20.6% by wt.
Slack wax yield	16.8% by wt.

	Filtrate.	Extract.	Slack wax.
Sp. gr. at 60° F	0.868	0.971	0.817
Flashpoint (P.M. closed), ° F	415	405	405
Red. I. visc at 140° F, sec.	64	122	—
Pour point, ° F	20	65	—
Acidity, MgKOH/gm	—	—	—
Wax content, % by wt	—	—	—
Colour (A.S.T.M.)	1	—	—
Visc (Kin) at 100° F, cs	32.2	—	—
" 210° F, cs	5.12	—	—
Visc index	94	—	—

Melting point of slack wax, ° F	125
" pure wax, ° F	128
Refr. index at 60° C of slack wax	1.4390
" pure wax	1.4360
" oil	1.4660
Oil content of slack wax, %	11

#### Pool 8 Distillate.

Pool 8 distillate was a blend of Pool 11 and Pool 12 distillates

Finished grade	Pool 8.
Solvent treatment	225% of 90% SO <sub>2</sub> /10% benzol. 3 stage 25/45° C.
Solvent dewaxing	Dilution 2.1/1. Solvent 15% SO <sub>2</sub> /85% benzol (by wt.).
Filtrate yield	63.2% by wt.
Extract yield	20.8% by wt.
Slack wax yield	16.0% by wt.

	Filtrate.	Extract.	Slack wax.
Sp. gr. at 60° F . . . . .	0.885	0.987	0.842
Flashpoint (P.M. closed), ° F . . . . .	445	395	410
Red. l. visc at 140° F, sec . . . . .	121	91 (200° F)	—
Pour point, ° F . . . . .	20	65	—
Acidity, MgKOH/gm . . . . .	0.03	—	—
Visc (Kin) at 100° F, cs . . . . .	83.2	—	—
"    210° F, cs . . . . .	8.92	—	—
Visc index . . . . .	86.4	—	—
Colour (Lovibond 1 in cell) . . . . .	10.0Y/1.5R	—	—

Melting point of slack wax, ° F . . . . .	131
"    pure wax, ° F . . . . .	140
Refr. index at 60° C of slack wax . . . . .	1.4500
"    pure wax . . . . .	1.4412
"    oil . . . . .	1.4715
Oil content of slack wax, % . . . . .	28

*Pool 11 Distillate.*

Finished grade . . . . .	Pool 11.
Solvent treatment . . . . .	100% of 85% SO <sub>2</sub> /15% benzol. 3 stage at 25/45° C.
Solvent dewaxing . . . . .	Dilution 1.3/1. Solvent 15% SO <sub>2</sub> /85% benzol (by wt).
Filtrate yield . . . . .	65.6% by wt.
Extract yield . . . . .	17.6% by wt.
Slack wax . . . . .	16.8% by wt.

	Distillate.	Filtrate.	Extract.	Slack wax.
Sp. gr. at 60° F . . . . .	0.892	0.883	1.009	0.827
Flashpoint (P.M. closed), ° F . . . . .	465	450	450	425
Red. l. visc at 140° F, sec . . . . .	96	104	97 (200° F)	—
Pour point, ° F . . . . .	100	20	30	—
Acidity, MgKOH/gm . . . . .	0.03	—	—	—
Colour (A.S.T.M.) . . . . .	—	2	—	—
Visc (Kin) at 100° F, cs . . . . .	—	67.2	—	—
"    210° F, cs . . . . .	—	7.77	—	—
Visc index . . . . .	—	85.5	—	—

Melting point of slack wax, ° F . . . . .	138
"    pure wax, ° F . . . . .	142
Refr. index at 60° C of slack wax . . . . .	1.4415
"    pure wax . . . . .	1.4380
"    oil . . . . .	1.4755
Oil content of slack wax, % . . . . .	12

*Pool 12 Distillate.*

Finished grade . . . . .	Pool 12b.
Solvent treatment . . . . .	250% of 85% SO <sub>2</sub> /15% benzol. 3 stage at 35/50° C.
Solvent dewaxing . . . . .	Dilution 2.0/1. Solvent 10% SO <sub>2</sub> /90% benzol (by wt).
Filtrate yield . . . . .	63.0% by wt.
Extract yield . . . . .	20.3% by wt.
Slack wax . . . . .	16.7% by wt.

	Distillate.	Filtrate.	Extract.	Slack wax.
Sp. gr. at 60° F . . . . .	0.902	0.886	1.003	0.852
Flashpoint (P.M. closed), ° F . . . . .	490	490	475	490
Red. I. visc at 140° F, sec . . . . .	215	196	254 (200° F)	—
Pour point, ° F . . . . .	115	25	55	—
Acidity, MgKOH/gm . . . . .	0.03	—	—	—
Wax content, % by wt . . . . .	13	—	—	—
Colour (A.S.T.M.) . . . . .	—	4—	—	—
Visc (Kin) at 100° F, cs . . . . .	—	146.0	—	—
Visc " 210° F, cs . . . . .	—	13.0	—	—
Visc index . . . . .	—	88.5	—	—

Melting point of slack wax, ° F . . . . .	137
" pure wax, ° F . . . . .	140
Refr. index at 60° C of slack wax . . . . .	1.4555
" pure wax . . . . .	1.4465
" oil . . . . .	1.4760
Oil content of slack wax, % . . . . .	27

*Pool 13 Distillate.*

Finished grade . . . . .	Pool 13.
Solvent treatment . . . . .	400% of 85% SO <sub>2</sub> /15% benzol. 3 stage at 27/47° C.
Solvent dewaxing . . . . .	Dilution 2.5/1. Solvent 15% SO <sub>2</sub> /85% benzol (by wt).
Filtrate yield . . . . .	37.2% by wt.
Extract yield . . . . .	28.5% by wt.
Slack wax . . . . .	34.3% by wt.

	Distillate.	Filtrate.	Extract.	Slack wax.
Sp. gr. at 60° F . . . . .	0.910	0.888	0.995	0.869
Flashpoint (P.M. closed) ° F . . . . .	495	475	465	255
Red. I. visc at 140° F, sec . . . . .	266	243	222 (200° F)	—
Pour point, ° F . . . . .	110	15	60	—
Acidity, MgKOH/gm . . . . .	0.03	—	—	—
Colour (A.S.T.M.) . . . . .	—	3	—	—
Visc (Kin) at 100° F, cs . . . . .	—	188.3	—	—
Visc " 210° F, cs . . . . .	—	15.22	—	—
Visc index . . . . .	—	87	—	—

Melting point of slack wax, ° F . . . . .	130
" pure wax, ° F. . . . .	139
Refr. index at 60° C of slack wax . . . . .	1.4630
" pure wax . . . . .	1.4535
" oil . . . . .	1.4785
Oil content of slack wax, % . . . . .	38

*Finished Wax.*

The slack waxes up to Grade 12 were de-oiled by conventional sweating methods. As the waxes were solvent refined, a finishing clay treatment of 0.5 per cent clay was sufficient.

Slack waxes were blended and sweated according to the wax grades required.

The finished wax was slabbed in a 1-ton capacity slabbing machine.



	Grade 5 H.P.	Grade 6 H.P.	Grade 7 H.P.
Sp. gr. at 60° F . . . . .	0.818	0.817	0.816
Setting point (I.P.), ° F . . . . .	142.3	138.0	134.9
Colour (Lovibond 5 in cell) . . . . .	0.2Y	0.4Y	0.3Y
Flashpoint (P.M. closed), ° F . . . . .	445	440	445

### *Duosol Treatment and M.E.K. Dewaxing.*

The vacuum residue from the distillation process was pumped over to the "Shell" Refining and Marketing Co. Ltd., Stanlow, where it was treated in their Duosol/M.E.K. Unit.

The operating results from this treatment have kindly been supplied for entry in this article.

"The indigenous vacuum residue received at Stanlow was extracted in the Duosol plant without any preliminary treatment. The extraction portion of the plant consists of eight extractors, the feed being introduced at No 3. Propane was introduced partly with the feed and partly at No. 1 extractor while selecto was introduced at No. 8. Extract and waxy raffinate were drawn off to the solvent recovery system at extractors 1 and 8 respectively.

"The data given below covers the processing at Stanlow of two typical grades of indigenous vacuum residue. Grade I was received up to approximately September 1944, and Grade II subsequently.

Analysis of feed.	Grade I.	Grade II.
Sp. gr. at 60° F . . . . .	0.923	0.933
Red. I. visc at 140° F, sec . . . . .	3340	5200
Flashpoint (P.M. closed), ° F . . . . .	435	505
Pour point, ° F . . . . .	70	75
Water content . . . . .	Trace	Trace
Salt content, % by wt . . . . .	0.025	0.025
Ash content, % by wt . . . . .	0.04	0.035
Solvent ratio (by wt.).		
Residue/Selecto/Propane . . . . .	1/5.3/3.8	1/5.0/4.0
Products.		
Waxy raffinate, % by wt . . . . .	51	49
Sp. gr. at 70° C/60° F . . . . .	0.852	0.855
Red. I. visc at 160° F, sec . . . . .	336	—
Flashpoint (P.M. closed), ° F . . . . .	460	485
(P.M. open), ° F . . . . .	485	565
Pour point, ° F . . . . .	105	—
Refr. index at 50° C . . . . .	1.4781	1.4795
Colour (Union) . . . . .	Dil 6 — (P —)	Dil 6 + (P +)
Wax content, % by wt . . . . .	20.0	21.0
Extract, % by wt . . . . .	49	51
Sp. gr. at 120° C/60° F . . . . .	0.953	0.956
Flashpoint (P.M. closed), ° F . . . . .	470	515
Penetration at 25° C . . . . .	280	109

"The waxy raffinate was treated by the MEK/Benzol process to remove wax, filtration being carried out in Vallez pressure filters.

Solvent Ratio (by vol.).	Grade I.	Grade II.
Feed/solvent . . . . .	1/4.0	1/4.2
Feed/cold wash . . . . .	1/1.6	1/1.6
Products.		
Dewaxed raffinate, % by wt. . . . .	77	77
Sp. gr. at 60°/60° F . . . . .	0.8905	0.893
Flashpoint (P.M. closed), ° F . . . . .	475	495
" (P.M. open), ° F . . . . .	505	550
Red. I. visc. at 140° F, sec. . . . .	609	992
" 200° F, sec . . . . .	162	—
Visc (Kin) at 100° F, cs . . . . .	570.0	934.8
" 210° F, cs . . . . .	32.8	44.54
Visc index . . . . .	95	96
Pour point, ° F . . . . .	10	10
Colour (Union) . . . . .	Dil 6 — (P —)	6 — (P —)
Slack wax, % by wt. . . . .	23	23
Sp. gr. at 70° C/60° F . . . . .	0.829	0.832
Flashpoint (P.M. closed), ° F . . . . .	495	490
Congeaing point (I.P. 76/44T), ° C . . . . .	60	60
Wax content, % by wt . . . . .	88.2	86.6

"The dewaxing raffinates shown above were treated with 3 per cent activated earth and 0.06 per cent lime at 240° C with steam.

Analysis of final product.	Grade I.	Grade II.
Sp. gr. at 60°/60° F . . . . .	0.889	0.891
Flashpoint (P.M. closed), ° F . . . . .	470	480
" (P.M. closed), ° F . . . . .	500	540
Red. I. visc. at 140° F, sec . . . . .	570	920
Visc (Kin) at 100° F, cs . . . . .	557.4	870
" 210° F, cs . . . . .	32.25	43.4
Visc. index . . . . .	95	96
Pour point, ° F . . . . .	10	10
Colour (Union) Dil . . . . .	5(0)	5(0)
B.A.M. oxidation test.		
Coke No. before . . . . .	0.42	0.57
" after . . . . .	1.01	1.22
" increment . . . . .	0.59	0.65
Loss on treatment, % by wt. . . . .	3	3

"The finished oil was absorbed into Air Ministry lubricating oil production."

### *Dubbs Cracking.*

The cracking plant was a modern U.O.P. cracking, polymerizing and gasoline treating combined unit built during the first year of the war and sufficiently covered in the literature to require no description here.

It was operated to even out the load and consequently operated on a wide variety of raw oil from indigenous crude oil down to the highly viscous, indigenous vacuum residue. Extracts, foots oils, unsweatable slack waxes and such products were cracked to motor spirit and fuel oil when they were out of line with market requirement.

Cracking data on a typical mixed cracking stock are given below :—

Raw oil    Approx.    70% slack wax and lube oil distillate  
                              18% lube oil extract.  
                              12% vacuum residue.

#### Analysis of Raw Oil.

Sp. gr. at 60° F	0.900
Flashpoint (P.M. closed), ° F	370
Red. I. visc at 140° F., sec	95
% vol. at 400° F	2
Pour point, ° F	95

#### Products.

Cracked gasoline	40.3% by wt on charge.
Sp. gr. at 60° F	0.7220
Colour (I.P.)	W. white
Reid vapour pressure	14.5
Octane No. (A.S.T.M.)	74
I.P. distillation :	
I.B.P., ° C	31
10% vol. at ° C	61
20%   "   "	77
30%   "   "	92
40%   "   "	106
50%   "   "	116
60%   "   "	130
70%   "   "	142
80%   "   "	156
F.B.P., ° C	171
Residuum	46.8% by wt on charge
Sp. gr. at 60° F	1.015
Red. II. visc at 140° F, sec	50
Flashpoint (P.M. closed), ° F	170

Cracking was operated for high R.V.P. gasoline to bring up the R.V.P. of the straight-run on subsequent blending.

#### GENERAL.

During the years covered by this report, 1942 to 1945, the following tonnages of major finished products were supplied from indigenous crude oil by Lobitos to the war effort :—

Motor spirit	47,600
White spirit	18,300
DERV	107,900
Lubricating oils	30,000
Paraffin wax	4,300

These products went into the common pool distributed by the Petroleum Board. Their eventual history is part of the history of the co-operative effort put forward by the petroleum industry as a whole. In that history it will be found that these indigenous products played no small part in fuelling and lubricating the war machines. Their more obvious usefulness in saving ship miles is apparent from the tonnages involved.

For those interested in enemy action it is sufficient to state that the near miss on the rail sidings, which occurred prior to the first receipt of indigenous crude oil, was the last recorded incident in the area.



The author would express his thanks to the Petroleum Board and Lobitos Oilfields Ltd., for their permission to utilize the data recorded, to the Anglo-Iranian Oil Co. Ltd., for permission to publish data relative to their crude oil and to the "Shell" Refining and Marketing Co. Ltd., for supplying their operational results on the solvent treatment and solvent dewaxing of indigenous vacuum residue.

## EXPLOSIVE DECOMPOSITION OF ETHENE.

By H. I. WATERMAN, W. J. HESSELS, and J. VAN STEENIS.

IPATIEV<sup>1</sup> was the first investigator to polymerize ethene under high pressure and at high temperatures, without a catalyst. He, however, did not report any explosions occurring in this reaction.

Later it was reported that ethene under the conditions mentioned above (about 200 atm and 350° C) *may* decompose into its elements, this reaction having an explosive character.<sup>2,3,4,5</sup> Dunstan, Hague, and Wheeler<sup>5</sup> state that the material of the reaction autoclave has a marked influence upon this decomposition.

Afterwards Hessels, van Krevelen, and Waterman<sup>6</sup> found that the polymerization of ethene, with aluminium chloride as a catalyst, is promoted by finely divided nickel. This promoting agent also gives rise to a vigorous reaction at room temperature and about 60 atm pressure. Under these circumstances it is also possible that explosions occur. One of us (W. J. Hessels) had this experience twice during experiments in the research mentioned above.

During a research in this laboratory it was found that some *solvents* for the aluminium chloride also have a promoting action on the polymerization of olefins.<sup>7</sup>

If, however, the starting pressure of ethene is about 40 atm in this case, an explosion may result even at temperatures as low as 0° C.

A lower starting pressure (20 atm) also gives rise to a vigorous reaction in the beginning, which, however, now can be kept under control, *e.g.* :

(1) 200 g of aluminium chloride,<sup>8</sup> 150 g of nickel on a support of kieselguhr and 200 ml of pentane were introduced into a 2-litre autoclave; 60 atm of ethene were added at 18° C. The temperature increased within a few minutes to 330° C, upon which the autoclave-head was lifted to a small extent. After this explosion a pressure of 450 atm was recorded.

The reaction residue consisted for the greater part of a soft coal-like mass. Some ethene polymers were also formed.

(2) To 10 g of aluminium chloride<sup>8</sup> and 100 ml of methylchloride at -20° C, ethene was introduced to 30 atm. Slowly warming up of the reaction-autoclave to about -5° C (pressure 40 atm) caused an instantaneous increase of pressure and temperature, which in a few seconds caused an explosion, completely destroying the manometer of the autoclave.

The reaction product was a soft coal-like mass, which still contained aluminium chloride.

(3) A similar experiment with half the amount of aluminium chloride and a starting pressure of 20 atm of ethene, at the same temperature as before, showed a sudden increase of pressure to more than 100 atm, after which a fast pressure drop to 0 atm followed. Additional introduction of ethene to 20 to 30 atm and temperatures

from 0° to 10° C, on the contrary caused a relatively slow decrease of pressure, the ethene being polymerized to liquid reaction products. Probably the activity of the aluminium chloride is noticeably diminished by the vigorous reaction in the beginning.

(4) 10 g of aluminium chloride dissolved into 20 ml of nitromethane showed at room temperature no appreciable reaction with ethene at 30 atm pressure. Slowly warming up the reaction autoclave to about 30° C gave an unexpected temperature increase. The heating was stopped (45° C, 38 atm). The temperature, however, still increased until at 75° C an explosion followed, again destroying the manometer, and leaving some soft coal-like mass.<sup>9</sup>

The experience described above, emphasizes that the utmost care is needed in working with ethene even under comparative small pressure and low temperature conditions.

*Delft, Laboratory for Chemical Engineering of the Technical University,  
November 20, 1946.*

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- <sup>7</sup> Unpublished experiments with ethene carried out by M. Caviet.  
Unpublished experiments with *isobutene* carried out by R. Jonckheer.
- <sup>8</sup> The aluminium chloride from experiment 1 was a technical product, in the other experiments it was prepared from aluminium and dry hydrogen chloride gas.
- <sup>9</sup> Experiment carried out by P. W. Pfeiffer.



# THE OXYGEN BOOST METHOD OF RATING THE ENGINE PERFORMANCE OF AVIATION FUELS.

By W. B. HEATON \* (Fellow), T. K. HANSON \* (Fellow), and  
R. C. MORRIS.\*

## INTRODUCTION.

OF all the natural problems which have confronted the petroleum technologist and the automotive engineer, the type of hydrocarbon combustion associated with knock appears to have been, and still to be, the most formidable. A very considerable proportion of the development organizations of both oil companies and engine manufacturers has been devoted to the study of this phenomenon, to the production of fuels with lesser tendencies to knock and to the production of combustion chambers and engines to give the maximum power output when utilizing a given fuel.

Although a very large volume of fundamental work on the combustion reactions associated with knock has been carried out, it must be admitted that progress in the production of higher quality fuels and in designing engines to use these fuels has been made for the most part by empirical methods.

The corner-stone in the empirical edifice, which has been erected to cope with this vast problem, has been the series of laboratory methods of rating fuels with regard to knocking characteristics.

It is proposed to describe a method of engine testing which, although now mainly of historical interest, may serve to indicate how a satisfactory test procedure may be evolved to deal with a specific problem without elaborate equipment and in the minimum time.

In the late thirties, two methods of knock rating of aviation fuel were in use, the 1-C method in the U.S. and the motor method in the U.K. A modification of the latter method had been specified by the British Air Ministry but was abandoned just before the war. Both these methods of test operated at maximum knock-mixture strength, *i.e.*, at a fuel-air ratio not far removed from that which obtains in an aero-engine when operating under cruising conditions. At this time considerable attention was being paid to the increase in knock-limited power output which could be obtained at rich-mixture strength. A method of rating aviation fuels was evolved using a Bristol Pegasus single-cylinder engine. Fuels were rated by measuring the knock-limited power output at various increments of increasing mixture strength up to a peak which was obtained in the rich-mixture response curve. The peak b.m.e.p. of a selected 100-octane fuel was chosen as the reference point and the rating of the fuel expressed as

$$\frac{\text{peak b.m.e.p. of test fuel}}{\text{peak b.m.e.p. of reference fuel}} \times 100.$$

The reference fuel was designated B.A.M. 100.

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A rich-mixture rating of 100 was required for 100-octane fuel supplied to the Air Ministry, although this clause in the specification was not published at the time. The Bristol Pegasus test proved to be most satisfactory in operation and the results obtained were for the most part reproducible; obviously, however, such a test could not be used for control purposes at the refinery or during shipping and distribution. Furthermore, such a test was ill-suited for use in connexion with the development of aviation fuels of high rich-mixture rating on account of the comparatively large quantity of fuel required.

At the request of the Engine Sub-Committee of the M.A.P. Fuel Committee in August 1940, a combined research project was launched on the development of a supercharged laboratory engine, the rich-mixture ratings of which would correlate with those of the single-cylinder Bristol Pegasus engine.

By supercharging and employing fuel injection, and by incorporating various modifications to enable the engines to withstand the more severe operating conditions, engines were evolved, which, in a few cases, correlated reasonably well with the Pegasus engine.

It was felt that too much stress was being placed on the engineering aspect, when the actual fuel ratings obtained were of more value; also, it seemed essential that, apart from being able to correlate with the single-cylinder Pegasus, an engine should have the following characteristics:—

- (1) Simplicity of adaptation from existing knock-rating equipment;
- (2) Simplicity of operation;
- (3) Use of a minimum number of operators;
- (4) Use of a minimum quantity of fuel.

Bearing in mind the urgency of the project, items (1) and (2) were of importance if the engine were to be modified or erected and operated on the refinery. With reference to item (4), the rapidity with which a research programme can be carried through depends to a great extent on the minimum quantity of sample required.

As an alternative to supercharging the C.F.R. engine with compressed air the proposal to use oxygen directly from a cylinder appeared attractive. Rich-mixture response curves could then be obtained by plotting the rate of flow, limited by knock, of the added oxygen against the rate of fuel flow.

Other workers in this field had obtained correlation with engine conditions varying between the following limits:—

Speed . . . . .	1500–2400 r.p.m.
Inlet air temperature . . . . .	100–200° C
Jacket temperature . . . . .	100–180° C

The following modifications were then made to a standard Motor Method (F.2) C.F.R. engine:—

- (a) The 900 r.p.m. pulley on the synchronous alternator was changed for a 1200 r.p.m. pulley;
- (b) The shrouded inlet valve was replaced by a plain exhaust valve;
- (c) F.3 large diameter valve springs were fitted;

- (d) An 18-mm A.C. spark plug, type RZ10/1R, was found to have the required heat range and was used in the early stages.
- (e) An F.3 method extension to the coolant condenser was fitted;
- (f) An F.3 method carburettor choke, size 0.750 in, was fitted;
- (g) The size of the metering jets was increased to 0.052 in;
- (h) The fuel tank and float chamber assembly were modified so that rates of fuel flow could be determined. This was achieved as shown in Fig. 1, by screwing a needle valve seating into the passage

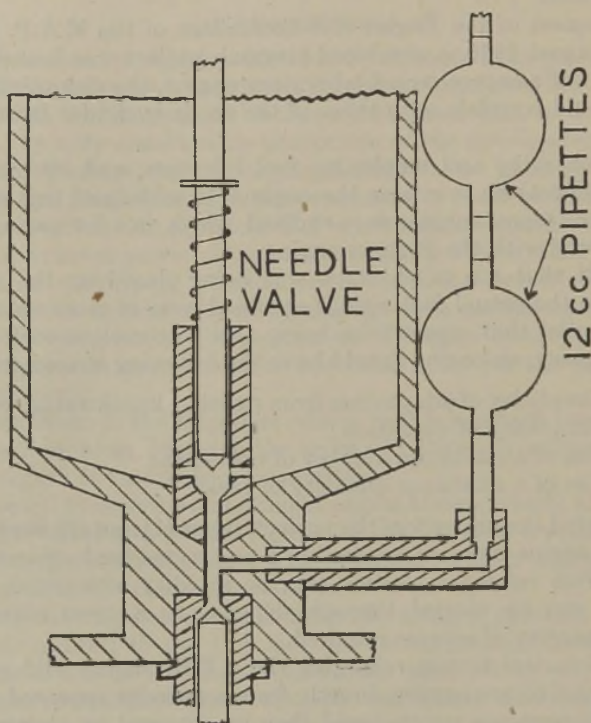


FIG. 1.

FUEL TANK MODIFICATION.

connecting the fuel tank with the float chamber. The needle valve which engaged this seat, was carried up through the top of the fuel tank and was held away from the seating by a light spring. The fuel tank was drilled so that on closing the needle valve, fuel flowed only from an external pipette made with two bulbs of 12 c.c. capacity;

(i) The inlet air, preheated by the earlier type F.3 300-watt heater, was drawn through a 5-gal mixing tank into the side of which the oxygen line was connected. The oxygen flow was controlled by a needle valve and measured by a simple orifice meter;

(j) The bouncing-pin hole was closed by a solid brass plug, which was later replaced by a pick-up unit of an R.A.E.-Mullard Detonation Meter.



After initial trials, the following operating conditions were selected :—

(1) Speed	1200 r.p.m.
(2) Jacket temperature	212° F
(3) Inlet air temperature	110° F.
(4) Mixture temperature	212° F.
(5) Ignition timing	30° E
(6) Compression ratio	7.25 : 1
(7) Valve clearance (cold)	inlet 0.008 in
" " exhaust	0.012 in.

A jacket temperature of 212° F was preferred in order to give increased life to the exhaust valve seat.

It was hoped that the use of oxygen would so accelerate the rate of flame travel that correlation with the single-cylinder Pegasus engine would be obtained, even at the above low speed and jacket temperature.

After some weeks' operation, a few modifications were made and included :—

- (1) The increase of the inlet air temperature to 125° F in order to control more easily the mixture temperature;
- (2) The advancing of the ignition timing to 35° E as this gave slightly better correlation;
- (3) The change of plug type to Lodge RS14R as the electrodes were less susceptible to lead fouling. It was found necessary to cool the plug with water when rating fuels above 105 performance number. Since the water cooling of the plug had no adverse effect on the correlation of lower performance number fuels, it was used continually;
- (4) An orifice meter reading to  $\pm 0.005$  cu.ft/min was installed;
- (5) A standard F.3 inlet air surge tank replaced the original mixing tank. The oxygen line was connected to a circular distribution ring fixed round the upper end of the inlet air pipe within the surge tank.

### TEST PROCEDURE.

A mixture response curve was obtained by fixing the fuel flow in successive stages and increasing the oxygen flow until the point of incipient knock at each stage was found. At each stage the fuel flow and oxygen flow were determined. As the mixture strength was increased, so was the current to the mixture heater.

One operator was required and he could determine up to sixteen ratings, excluding checks on the reference fuels, in an eight-hour day.

Two litres of fuel was ample for a full mixture response curve, though one litre sufficed when the approximate rating of a fuel was known.

Day to day reproducibility of the reference fuel curves was satisfactory, being equal to  $\pm \frac{1}{2}$  a performance number in the critical region of the constant specific fuel consumption rating line (Fig. 5).

The need for valve seat maintenance was usually indicated by a sudden rise in the peak of the 100-performance number reference fuel and the lack of compression on stopping the engine. Periods between overhauls were as long as 100 hours, although the average period approximated to 75 hours.

The first series of results are shown in Fig. 2. The fuels tested were a series of correlation fuels specially selected to represent a wide variety of fuel types.

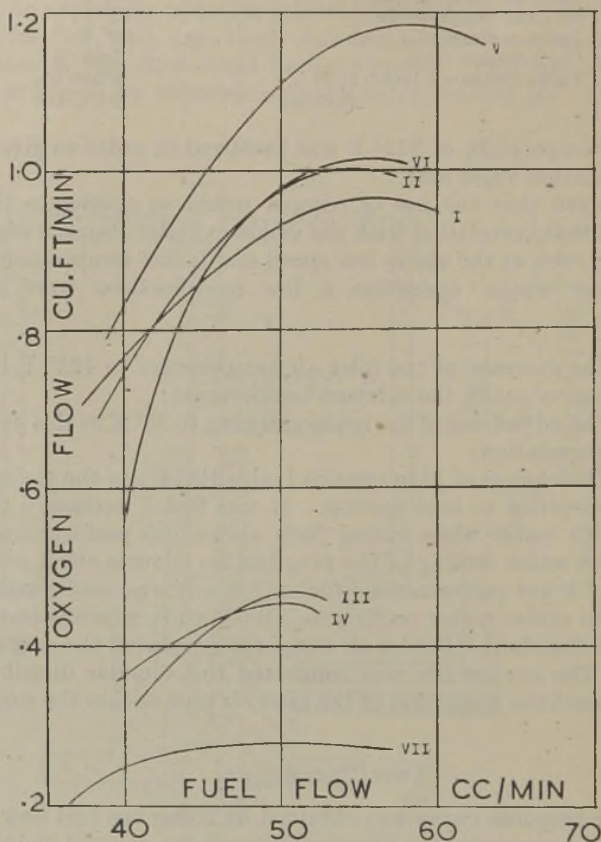


FIG. 2.

RICH MIXTURE RESPONSE CURVES OF CORRELATION FUELS.

Operating conditions :

Comp. ratio . . . . .	7.5 : 1
Ignition . . . . .	30° E
R.p.m. . . . .	1200
Mixture temp. . . . .	100° C
Jacket temp. . . . .	100° C

Fuels : A.M.C. series.

#### THE DETERMINATION OF PERFORMANCE NUMBERS.

At the time when these tests were being carried out, Pegasus performance numbers were calculated in terms of the peak b.m.e.p. of both test and reference fuels, irrespective of the fuel consumption at which these peaks occurred. If, therefore, there was a linear relationship between the peak

oxygen flow and Pegasus performance number, then the oxygen addition method of determining performance numbers could be used. This linear relationship is shown in Fig. 3.

It was, however, suggested that, as 100-octane fuels would, in service, be used in engines having fixed carburettor settings independent of the fuel type, it would be more satisfactory if all fuels were rated at the same specific fuel consumption, this fuel consumption corresponding to the peak

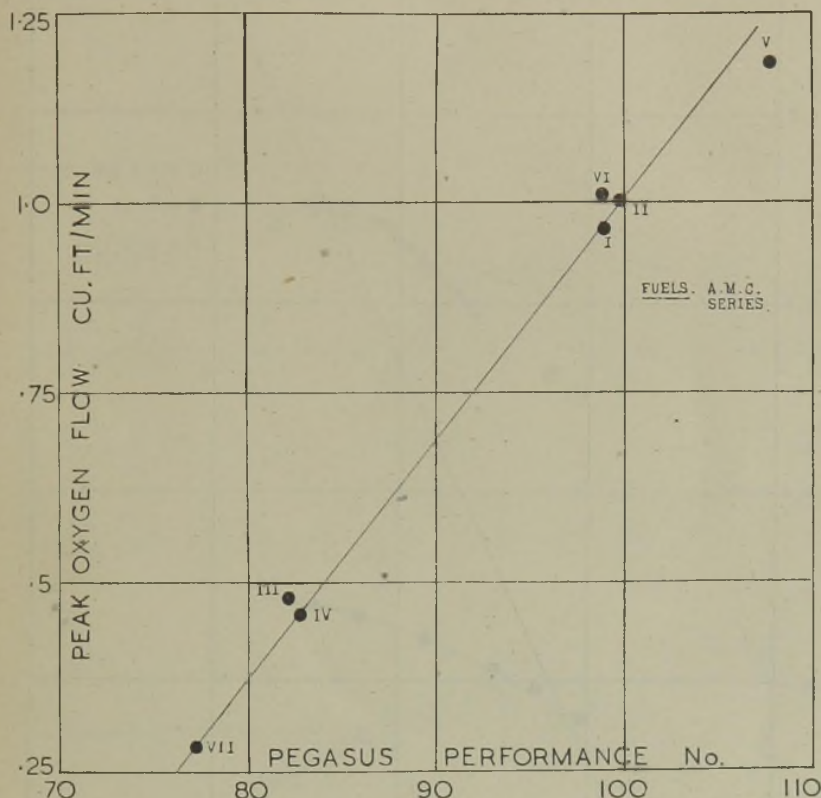


FIG. 3.

LINEAR RELATIONSHIP BETWEEN PEAK OXYGEN FLOW AND PEGASUS PERFORMANCE NUMBER.

of the 100-octane reference fuel. This method tended to restrict development of fuels outside the 100-octane range for which carburettor settings other than those used for 100-octane fuels might be desirable. However, owing to the general similarity in the shape of mixture response curves, this objection to the proposed method of rating was not really serious.

In order to bring the results obtained by the oxygen addition engine into line with those obtained by the latter method with the single-cylinder Pegasus, a constant specific fuel consumption rating line on the rich mixture response curve had to be obtained.



The method used was to determine the rich-mixture response curves of two reference fuels by plotting oxygen flow against fuel flow. The fuels chosen were Air Ministry Reference Fuel B.A.M. 100 and Air Ministry correlation fuel A.M.C.VII, as they were available in bulk. Their Pegasus

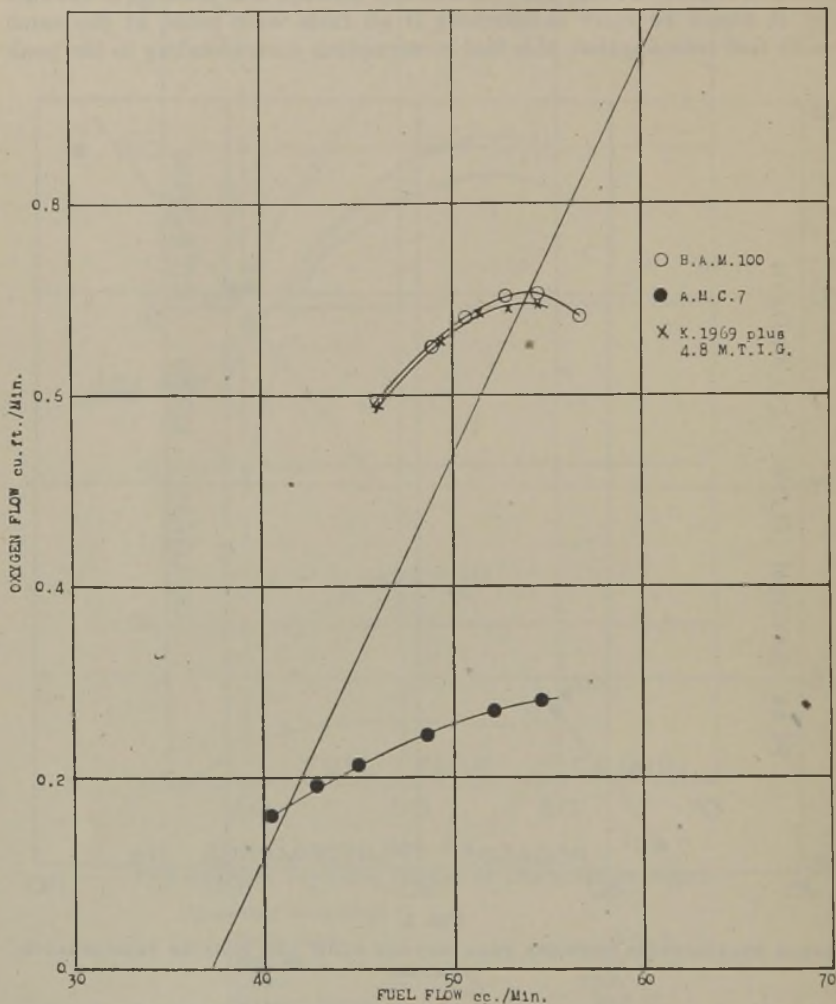


FIG. 4.  
RICH MIXTURE RESPONSE CURVES AND RATING LINE.

performance numbers were 100 and 76.3 respectively. A line was then drawn between the points :—

(a) The peak of B.A.M. 100

and

(b) A point on the A.M.C.VII curve at which the fuel consumption was  $0.763 \times$  the peak fuel consumption of B.A.M. 100.

This line is shown in Fig. 4 and is referred to below as the rating line. Performance numbers could be determined from the formula

$$76.3 + \frac{X - B}{A - B} \times (100 - 76.3)$$

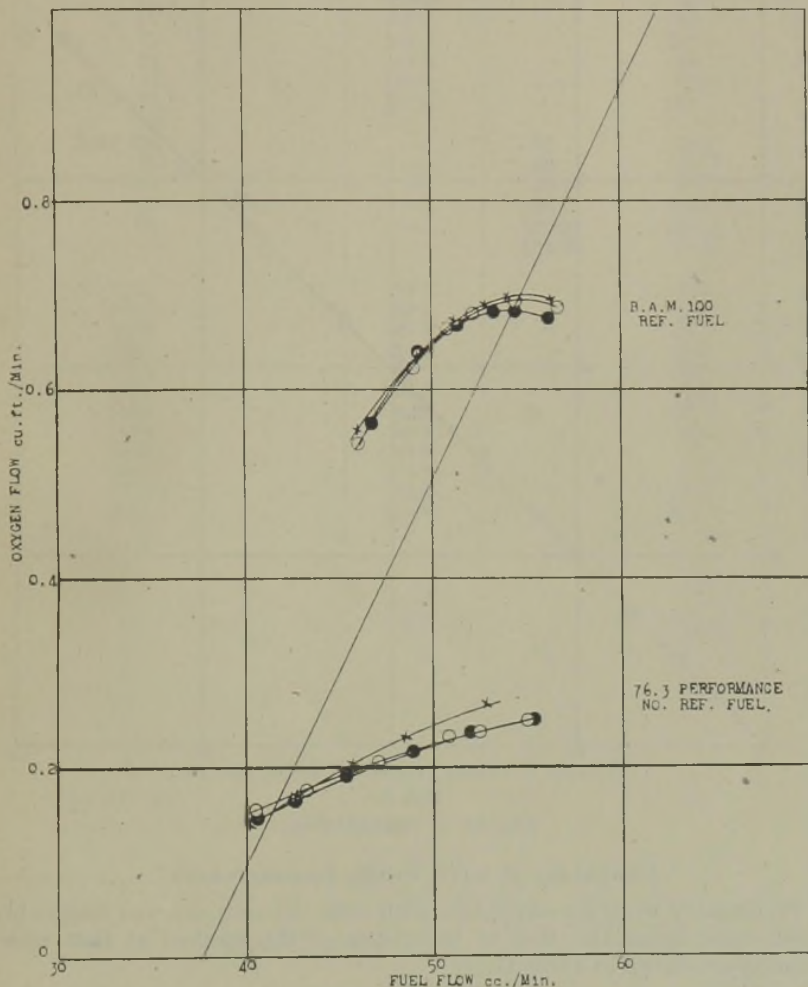


FIG. 5.

DAY TO DAY REPRODUCIBILITY OF REFERENCE FUEL CURVES.

where  $X$  is the oxygen flow at the point where the mixture response curve cuts the rating line, and  $A$  and  $B$  are the corresponding oxygen flow rates of B.A.M. 100 and A.M.C.VII respectively.

However, in practice, the performance numbers were determined graphically.

## CORRELATION WITH PEGASUS AND HERCULES SINGLE CYLINDER ENGINES.

Table I and the graph in Fig. 6 show the degree of correlation which was obtained with the Pegasus and Hercules engines. The Hercules ratings are included since they correlated well with the Pegasus.

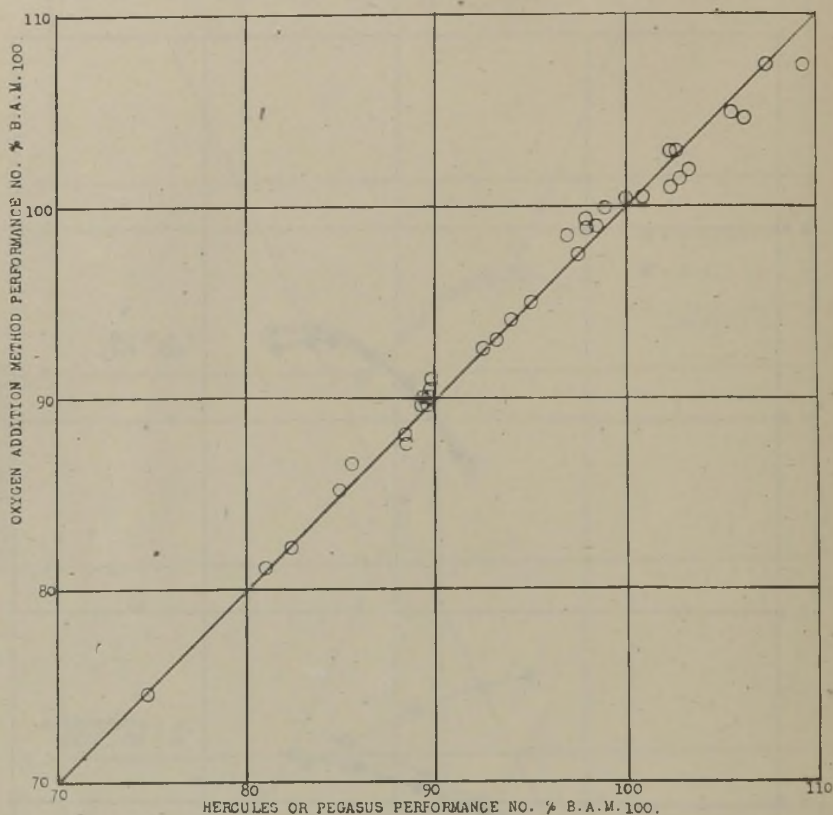


FIG. 6.

DEGREE OF CORRELATION.

## CORRELATION WITH OTHER LABORATORIES.

Preliminary work on correlation with other laboratories was reasonably good, considering the lack of experience of the method at that time. Results are shown in Table II.

## ACKNOWLEDGMENTS.

The authors wish to thank the directors of Trinidad Leaseholds Ltd for permission to publish this paper and desire to acknowledge the assistance of P. L. Molyneux, Trinidad Leaseholds Ltd, who carried out a considerable number of the ratings, and also the M.A.P., Esso European, A.I.O.C., Thornton Engine, I.C.I., U.O.P. and Standard Oil Development Co. laboratories for their participation in the development of this method.



TABLE I.  
Performance Numbers, % B.A.M. 100 Reference Fuel.

Fuel.	Pegasus.	Hercules.	Oxygen method.
AMC. I . . .	98	—	99.5
III . . .	80.8	—	81
IV . . .	82.2	—	82
V . . .	109.5	—	107.5
VI . . .	98.3	—	99
VII . . .	76.3	—	76.3
VI.D . . .	102.5	—	103
AMC. 30 . . .	—	97	98.5
31 . . .	—	98	99
32 . . .	—	98.75	99.5
33 . . .	—	100	100.5
34 . . .	—	103.5	102
35 . . .	—	104.75	106.5
K. 1581 . . .	89.3	=	90
1582 . . .	89.7	—	90.5
1583 . . .	89.5	—	90.1
1584 . . .	88.4	—	88
1625 . . .	88	—	89
1627 . . .	85.5	—	86.5
1628 . . .	80.8	—	81
1629 . . .	85.8	—	86
1630 . . .	89.3	—	91
1631 . . .	92.5	—	92.5
1634 . . .	98.5	—	100
1635 . . .	102.5	—	101
R.S. 76 . . .	94	—	94
A.I. 1 . . .	93.2	—	93
2 . . .	98.5	—	99
3 . . .	—	101	100.5
4 . . .	—	95	95
5 . . .	—	97.5	97.5
6 . . .	—	107.5	107.5
7 . . .	—	105.75	105
8 . . .	—	102.75	103
9 . . .	—	101	101
D.T.D. 230 . . .	—	74.5	74.2

TABLE II.

Fuel.	Pegasus.	Hercules.	Oxygen method.			
			C.L.	Trinidad.	U.O.P.	S.O.D. Bayway.
AMC. I . . .	98	—	99.5	99	97	98.5
III . . .	80.8	—	81	—	81.5	—
IV . . .	82.2	—	82	—	82	81.8
V . . .	109.5	—	107.5	108.5	107	113
VI. D . . .	102.5	—	103	—	—	103.5
A.I. 10 . . .	—	97.5	97.5	97.5	97	—
11 . . .	—	95	96, 97	94.7	95	—
12 . . .	—	—	—	101.7	101	—

## OBITUARY.

## ING. DR. LEO STEINSCHNEIDER.

We regret to announce the death of Leo Steinschneider, which occurred on October 10, 1946, in a private nursing home. He was 73.

Born in Prostějov, Moravia, Czechoslovakia, he studied engineering at the Technical High School, Vienna, where he graduated engineer, and soon afterwards entered the service of the Brünn-Königsfelder Maschinenfabrik, Bruenn-Koenigsfeld (Brno-Kralovo Pole), Czechoslovakia. He was made a director of the firm in 1915 and remained associated with it until 1939.

As chief engineer of the oil refinery equipment branch of the engineering works named he developed and patented a high vacuum distillation plant, which was extensively adopted by the major oil companies in both hemispheres. In 1912 he delivered a lecture at the Eighth International Congress of Applied Chemistry at the Columbia University, New York, on that process of distillation, and a paper on the subject was read on his behalf before the Institution of Petroleum Technologists in 1925. A model of his high vacuum distillation plant was presented to the Science Museum, South Kensington.

Michael Leopold Steinschneider became a member of The Institution of Petroleum Technologists in 1926 and was elected Fellow of The Institute of Petroleum in 1939. During the past seven years he resided in this country, latterly at Oxford.

J. WALMSLEY.

## WALTER BERNOULLI, PH.D.

The sudden death on December 8, 1946, of Walter Bernoulli, president of the board and head of the geological department of the Museum of Natural History in Basle, is recorded with deep regret.

Born on May 23, 1885, in Basle, Walter Bernoulli studied geology at the Universities of Basle and Vienna and obtained his doctorate at Basle in 1911. In that year he became geologist to the British-Borneo and Burmah Petroleum Syndicate Ltd. and carried out work in British North Borneo and Brunei, and for the next three years was engaged in the same part of the world for the Bataafsche Petroleum Maatschappij. Later he was geologist to the Deutsche Erdöl A.G. operating in various European countries and subsequently, as chief geologist to the Cie Financière belge des Pétales, visited various parts of the world.

In 1935 Dr. Bernoulli became head of the geological department of the Museum of Natural History, Basle, a member of its board of directors in 1935, and its president in 1941. He became a Member of the Institute of Petroleum in 1926.