THE INSTITUTE OF PETROLEUM.

A meeting of the Institute of Petroleum was held at Manson House, Portland Place, London, W.1, on Wednesday, March 13, 1946. Mr. G. H. Coxon, Chairman of Council, presided.

THE CHAIRMAN, in introducing Dr. J. F. Walter, the author of the paper to be read, said that Dr. Walter had served with the P.A.W. on important war work, and was now with the Universal Oil Products Company. He was staying in London for a few months, and the members of the Institute were very glad to welcome him at their meeting.

The following paper was then read :—

DEVELOPMENTS IN FLUID CATALYTIC CRACKING.

By J. F. WALTER, D.Sc.*

THE contributions of catalytic cracking to the production of aviation gasoline and synthetic rubber during the war are so well known in the petroleum fraternity that to dwell on this subject is merely to repeat an oft-told story. However, it may be of interest to briefly describe the development of one type of catalytic cracking process by which a major share of war-time catalytic cracking was done, and, more important from the commercial view, to describe the outgrowth of some developments in fluid catalytic cracking as they apply to the post-war task of improving the quality of motor fuel and producing other desirable products from petroleum.

Those who have carefully followed the literature on catalytic cracking will recognize that certain portions of this exposition have been previously set forth in the literature. However, for the sake of completeness, and for those who may not be familiar with all the publications on the subject, it has been thought best not to omit these portions.

It soon becomes apparent to anyone seeking to develop a catalytic cracking process around one of the present commercially applicable cracking catalysts that the major part of his job is to devise a system by which the heat generated by the burning of coke from spent catalyst may be economically dissipated without raising the catalyst to such a temperature that its activity is seriously impaired. This problem of heat removal may be solved in a number of ways, but several companies doing development work on catalytic cracking before the war chose the use of a finely-divided catalyst which, when aerated with gas or vapour, could be made to flow like a fluid, as the most promising solution. With such a catalyst it became economically feasible to circulate sufficient catalyst through the regenerator to remove the heat of combustion of catalyst coke, except for that carried out by the flue gas and the relatively small

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* Universal Oil Products Company.

radiation loss, as sensible heat in the catalyst flowing from the regenerator, and at the same time to avoid excessive regenerator temperatures. Furthermore, this mechanism offers a simple method of transferring the major part of the heat of regeneration to the oil charge with which the regenerated catalyst is mixed.

The process looked so promising that several companies undertook to develop it co-operatively, and the first three commercial units, designed for
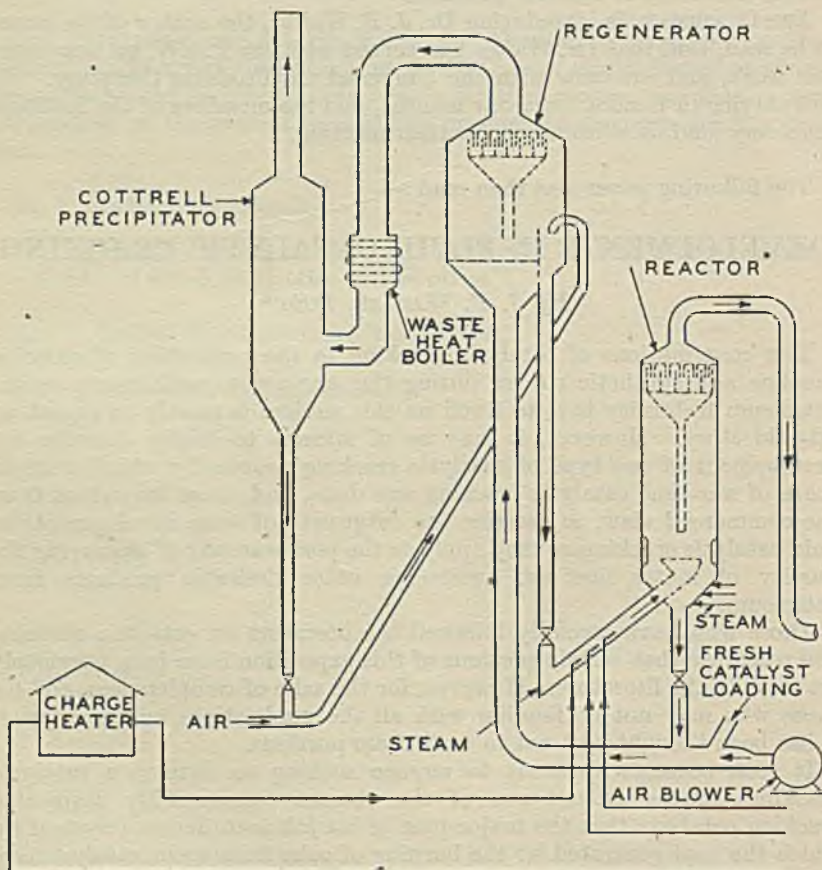

Fig. 1.
DOWNFLOW FLUID CATALYTIC CRACKING UNIT.

motor gasoline production, were under construction at the time the United States entered the war. These units, built by affiliates of the Standard Oil Company (N.J.), are of the so-called " up-flow design," in which spent catalyst is carried overhead from the reactor in the cracked oil vapours, is separated from the vapours by centrifugal separators, and then flows from a collecting hopper through a standpipe, at the bottom of which it is mixed with a stream of air and carried into the regenerator.

Regenerated catalyst is carried overhead from the regenerator by flue gas, and is collected by centrifugal separators and a Cottrell precipitator. The regenerated catalyst then flows from a collection hopper into a standpipe, at the bottom of which the hot catalyst is mixed with the oil charge and is transported into the reactor.

In these " up-flow " units the velocities of vapour in the reactor and air in the regenerator are such that no sharp gradient of catalyst concentration exists in either vessel.

Before these units were put into operation, however, marked economies were found in a " down-flow " design; therefore, with one exception, this modification of the process was adopted for all units then in the engineering stage and for all subsequent fluid catalytic crackers.

A schematic flow diagram showing the general arrangement of equipment for down-flow fluid catalytic cracking units built during the war for production of aviation gasoline is shown in Fig. 1.

Liquid charge stock is mixed with hot regenerated catalyst at the bottom of the regenerated catalyst standpipe, the heat content of the catalyst being sufficient to vaporize the oil and to supply the heat of cracking. The mixture of oil vapour and catalyst flows upward through a riser and into the reactor, where the vapour velocity is such that a layer of dense catalyst covers the grid plate. The oil vapours pass through this dense catalyst layer and enter a centrifugal separator, where the bulk of the entrained catalyst is removed. The cracked oil vapour then enters a fractionating tower, where the desired products are separated.

Catalyst carried into the fractionator is returned to the reactor system by recycling the total tower bottoms stream to the reactor or by passing the tower bottoms through a settler, decanting the catalyst-free oil, and mixing the catalyst concentrate with fresh oil and charging this mixture to the reactor.

Spent catalyst from the dense catalyst layer in the reactor is stripped with steam as it flows through the bottom section of the reactor and then descends through a standpipe to a point where air is introduced, and carries the spent catalyst through a riser into the regenerator, where the catalyst coke is burned in a stream of air supplied by a blower. Regenerated catalyst flows from the regenerator through a standpipe, at the bottom of which it joins the oil charge to the reactor. Some units were equipped with catalyst coolers external to the regenerator through which catalyst was circulated to remove excess heat.

Hot flue gas from the regenerator passes through a waste heat boiler and into a Cottrell precipitator, where entrained catalyst is removed. One unit designed by U.O.P. is equipped with a scrubber in place of the Cottrell precipitator. In this scrubber the flue gas is brought in contact with the fresh gas oil charge to the catalytic cracker, and the resulting catalyst-oil mixture is pumped to the reactor. This scrubber operates very satisfactorily, and loss of oil in the flue gas has been found to be very small.

As already mentioned, the major part of the heat of regeneration is transferred to the raw oil charge as sensible heat in the regenerated catalyst. With this mechanism it is possible to operate at high temperature in the reactor with little or no preheat in the raw oil charge. Since the production

of light olefins for the manufacture of high-quality aviation blending agents, synthetic rubber, and chemicals is improved by increasing reactor temperature in the normal range of operation, it is possible to obtain maximum yields of these light olefins from a fixed amount of charge stock. Towards this end the reactors of some fluid catalytic cracking units have been operated at 1000° F and above.

With a few exceptions the war-time fluid units were designed to operate with a pressure only slightly above atmospheric in the regenerator, although, if desired, this pressure could be raised somewhat. It was therefore necessary to mount the regenerator with its horizontal centre-line between 150 and 175 ft above ground level in order to provide sufficient head of catalyst in the regenerated catalyst standpipe to carry the catalyst into the reactor, where the minimum pressure is approximately 12 lb/sq. in., and to provide sufficient pressure drop across the regenerated catalyst slide-valve to assure control of catalyst flow. However, on one U.O.P.-designed unit the centre-line of the regenerator is mounted about 100 ft above ground level—at about the same height as the reactor—and the upper part of the regenerator carries a pressure of approximately 15 lb/sq. in. to provide the driving force necessary to move the catalyst from the regenerator into the reactor. This unit operates very satisfactorily, catalyst flow rates and levels being readily controlled.

SIMPLIFICATIONS IN DESIGN.

Analysis of the operating data and general experience gained by U.O.P. from fluid catalytic cracking units built during the war, as well as pilot-plant investigations carried out during the past several years, make it evident that simplifications and improvements in design can be made which will not only considerably reduce capital investment and operating costs, but will also improve liquid yield. The greatest simplification is achieved through the use of catalyst in the " microsphere " form, of which more will be said later.

Although this simplified fluid catalytic cracking unit for microspherical catalyst has been described in the literature,[1] it may be well to include a brief description here for the benefit of those who may not have seen the earlier publication and to round out this brief history of some developments in fluid catalytic cracking.

A schematic flow diagram of the simplified design is shown in Fig. 2. In the smaller units—up to 3500 to 5000 B/SD capacity—the reactor and regenerator are combined in a single column, the reactor in the top, the regenerator in the bottom. The liquid raw oil charge combines with hot regenerated catalyst flowing from the regenerator, and is vaporized, and the oil-catalyst mixture flows into the reactor. The oil vapour passes through three grids, each carrying a layer of dense fluidized catalyst, then passes through a centrifugal separator, where entrained catalyst is removed, and returned to the top layer of dense catalyst through a dip-leg. From the separator the cracked oil vapours pass to a fractionating tower of conventional design, where the desired liquid fractions are separated. The lower section of the column is refluxed with tower bottoms which circulate through a steam generator.

Where microspherical catalyst is used the catalyst content of the bottoms

is too small to warrant recycling to the reactor; therefore this fraction is sent directly to storage. When natural catalyst is used, however, it will usually be best to recycle part or all of the fractionator bottoms to the reactor in order to recover the contained catalyst.

Spent catalyst overflows from the top dense catalyst layer of the reactor into a stripper, where entrained oil and vapour are removed by a stream of stripping medium flowing countercurrently. At the bottom of the stripper
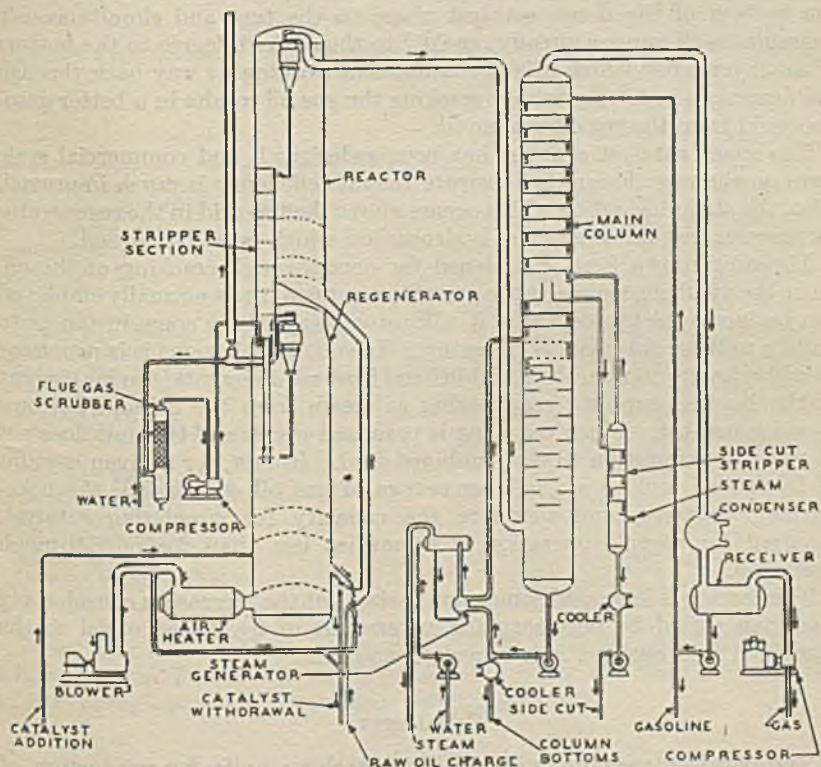

Fig. 2.

FLOW DIAGRAM MS-TYPE CATALYTIC CRACKING UNIT.

the catalyst enters a pipe, through which it flows into the top fluidized catalyst bed of the regenerator.

In the regenerator the dense mass of fluid catalyst is divided into three layers by grids. On the top layer, essentially oxygen-free flue gas from the lower part of the regenerator further strips the catalyst of hydrocarbons. The catalyst then drops to the second level, where part of the coke is burned at an intermediate temperature level by partially spent flue gas. At the third level the coke burning is completed at the maximum temperature with air, then the regenerated catalyst leaves the regenerator through a side draw-off fitted with a slide-valve to control the flow, thus completing the cycle.

Aside from the obvious simplification in design, with elimination of the heavy steel framework associated with older fluid units, and simplification of catalyst piping and catalyst recovery equipment, a number of improvements have been made in the internal construction of the vessels which will improve gasoline yields at a given gas oil conversion and will reduce the amount of coke which must be burned.

The grids in the reactor serve to prevent large-scale eddy motion in the dense catalyst phase, which rapidly carries partly cracked oil vapour from the bottom of the dense catalyst phase to the top, and simultaneously recirculates oil vapour already cracked to the desired degree to the bottom of the layer, after which it is overcracked in working its way back through the dense catalyst. Uniformly cracking the gas oil results in a better gasoline yield from the gas oil destroyed.

The spent catalyst stripper has been redesigned, and commercial scale tests on the new design demonstrate that its efficiency is much improved. Also, the stripping action which occurs above the top grid in the regenerator further reduces the amount of hydrocarbon which must be burned.

The unit shown here is designed for once-through cracking of the oil. Since the yield of gasoline at the gas-oil conversion levels normally employed can be increased by recycling, it will prove desirable in some instances to build a unit for this type of operation. In such installations it is necessary to add a heater to furnish the additional heat requirements, the major part of the heat so supplied reappearing as steam from the column bottoms steam generator. When recycling is practised the size of the unit does not increase in proportion to the combined feed. In fact, for a given amount of fresh feed and at a fixed percentage of gas oil conversion, the coke-burning capacity, and therefore the capacity for circulating catalyst, required for recycle operation is somewhat less than for once-through operation.

The reactor is increased somewhat in size, but the increase is considerably less than would be necessary for an amount of fresh feed equal to the combined feed charged in a recycle operation.

CATALYSTS.

The catalyst used in fluid catalytic cracking units for production of maximum quantities of aviation gasoline during the war was a finely ground synthetic silica-alumina preparation.

Synthetic silica alumina catalyst not only produces greater quantities of light hydrocarbons for alkylate and hydropolymer, but also yields an aviation base stock of higher quality than does the natural type. However, the search for improved catalysts carried out during the war in the U.O.P. laboratories led to two significant developments. According to the first of these, synthetic catalysts are produced in the form of very small spheres with high resistance to abrasion and fracture. These small spheres have come to be called microspheres. As compared to ground catalyst, the microspherical catalyst offers the advantages of considerably easier recovery, markedly reduced rates of attrition to extremely fine particles which are difficult to recover from process streams, and reduced erosion of lines and fittings in the plant.

The second development is a synthetic catalyst made up of silica and magnesia which produces markedly higher yields of gasoline than do either the synthetic silica-alumina or the natural catalyst. Octane numbers are, however, somewhat lower than for the other two catalysts, as may be seen from Table I, which shows a comparison of the yields from each of the three catalysts and the octane numbers of the catalytically cracked gasolines.

TABLE I.

Typical Yields and Product Qualities.

UOP MS-Typo Catalytic Cracking Processing Mid-Continent Gas Oil Once-through Operation at 65 per cent Conversion.

Catalyst.	Silica– Magnesia.	Natural.	Silica– Alumina.
Yields, vol. per cent :			
Debutanized 400° F e.p. gasoline	53·0	48·9	45·5
Cycle stock, 400° F +	35·0	35·0	35·0
Butylenes	5·5	5·8	6·2
Butanes	5·5	7·4	10·9
Propylene	3·8	4·8	6·8
Propane	1·9	3·4	3·7
C_2 and lighter gas, wt. per cent [*]	1·9	1·7	1·7
Debutanized, 400° F e.p. gasoline (5–6 cc R.v.p.) :			
Octane No. ASTM (F-2) :			
Clear	79·1	80·3	82·1
+ 3 cc TEL	85·2	86·5	87·7
Octane No. research (F-1) :			
Clear	89·0	90·8	93·0
+ 3 cc TEL	95·4	96·5	98·7
Cycle stock, 400° F + :			
Gravity, ° API	26	26	26
C_2 and lighter gas :			
Molecular weight	12	12	14
Heating value, BThU/cu. ft.	740	740	840

When any one of these three catalysts is used, a caustic treatment followed by inhibiting will usually suffice to bring the catalytic gasoline to final specifications on mercaptan content and gum.

FLUID CATALYTIC CRACKING AS A SOURCE OF RAW MATERIALS FOR CHEMICALS.

The bulk of chemical raw materials for which petroleum serves as a potential source is, of course, of two general types : aromatics and olefins.

Unfortunately, catalytic cracking is not a fertile source of that most-sought-after aromatic hydrocarbon, benzene. Toluene is produced in somewhat larger quantities, but it is doubtful if the cost of segregating it in high purity will make it competitive with that from other sources, except, possibly, for very large installations. When the fluid catalytic cracker is operated for a high percentage of gas-oil destruction with silica alumina catalyst, the fractions produced which boil above toluene in the gasoline range contain 70 per cent aromatics or more, and might be used for solvents in some applications.

An example of an analysis of a catalytic gasoline produced at high

conversion from a Coastal gas oil of 400° to 750° F boiling range, and a
U.O.P. characterization factor of 11·6, is shown in Table II.

TABLE II.

Yields from Catalytic Cracking of a Gas Oil with Silica–Alumina Catalyst at a High Conversion Level.

	Wt. per cent of gasoline.	Wt. per cent of fresh gas oil.
Benzene	3·4	1·0
Toluene	6·5	1·9
Xylene	10	2·9
Higher aromatics boiling up to 400° F	24	7·0

As mentioned before, the ability to circulate large amounts of catalyst
in fluid catalytic cracking units makes it possible to crack at a high reactor
temperature—1000° F or above when desired.   Since the yield of light
olefins is improved and the ratio of the olefins to paraffins in a given
boiling range can be markedly increased by raising reactor temperature in
the normal range of operation, this attribute of fluid crackers is a highly
useful one where light olefins for chemical manufacture are sought.

A tabulation of typical yields from the fluid catalytic cracking of a
30° A.P.I. Mid-Continent gas oil at 1000° F with silica-alumina catalyst

TABLE III.

Yields from Severe Fluid Catalytic Cracking with Silica–Alumina Catalyst, from Thermal Cracking of Gas Oil under Normal Conditions and from Severe Thermal Cracking of Gas Oil for the Production of Chemicals.

	Fluid catalytic cracking.	Normal thermal cracking.	Severe thermal cracking.
Charge.	Mid-Continent Gas Oil.		
Cracking temp., ° F	1000	890	1330
Yields, wt. per cent.			
Hydrogen	0·2	0·1	0·3
Methane	2·8	1·5	6·5
Ethylene	1·2	0·8	17·8
Ethane	1·3	3·7	8·6
Propylene	7·5	3·5	14·0
Propane	4·5	5·3	1·2
i-Butylene	2·3	1·0	2·4
n-Butylene	3·5	2·7	4·0
i-Butane	6·0	} 3·9	0·7
n-Butane	1·3		0·1
Butadiene	—	—	3·8
Amylenes	5·3	4·2	
i-Pentane	3·8	1·2	} 3·5
n-Pentane	0·6	2·8	
C₆—400° F fraction	26·5	44·8	20·1
Cycle stock	18·7	—	—
Heavy fuel	8·0	24·5	17·0
Coke	6·5	—	—
Total . . .	100·0	100·0	100·0

is shown in Table III. For purposes of comparison yields from thermal cracking of gas oil under normal conditions and for severe thermal cracking of gas oil are also included.

Higher yields of ethylene and propylene are obtained from severe thermal cracking than from catalytic cracking. However, as a competitor with severe thermal cracking for production of light mono-olefins for use as raw materials for chemicals, fluid catalytic cracking offers several advantages. It produces the desired olefins in relatively high concentrations in their respective fractions without converting a large percentage of the charge stock into other products for which there are no outlets through normal petroleum marketing outlets (products such as butadiene, penta-diene, styrene, etc.). While demands exist for many of these hydro-carbons, the fact remains that their segregation and purification require extensive facilities, which means that the most economical application of severe thermal cracking for manufacture of chemicals can be carried out only in conjunction with extensive and highly ramified chemical facilities.

Where diolefins find no use for production of chemicals or synthetic rubber, the production of mono-olefins in the C_4 and C_5 range by catalytic cracking offers the additional advantage that these olefins are not seriously contaminated by troublesome diolefins.

Aside from the application of the fluid process to catalytic cracking, it is also a solution to the problem, sometimes encountered in other fields than petroleum, of transporting large quantities of heat into or out of a reaction zone and the maintenance of that reaction zone at a uniform temperature. The process currently is applied to chemical production by one company in the United States.

SUMMARY.

To sum up, the experience with fluid catalytic cracking built up during the war, and laboratory and pilot plant developments of the past several years, have led to a considerably simplified design, with an attendant marked reduction in cost, improvement in gasoline yield, and reduced operating costs. Methods have been developed for forming synthetic catalysts into very small spheres, and catalyst in this form shows, when compared to ground catalyst, a considerably reduced rate of attrition to unrecoverable fines and an increased ease of recovery from gases or vapours.

Three compositions of catalyst are available for fluid cracking—namely, silica-alumina, natural, and silica-magnesia—the best catalyst for a given application being determined by the octane number of the gasoline which must be produced and by the requirements for raw materials for chemicals.

Since fluid catalytic cracking units are capable of cracking oil at high temperatures, and for this reason permit maximum production of light mono-olefins by the catalytic cracking route, its application to the production of light olefins for chemical manufacture should be investigated by those interested in this activity.

Literature References.

[1] Anderson, N. K., and Sterba, M. J., " The UOP MS-Type Catalytic Cracking Unit Meeting the Needs of the Smaller Refiner," *Petrol. Times*, 22.12.45, **49** (1263), 1080–1082.

DISCUSSION

THE CHAIRMAN said there were two questions which he would like to ask the author.

The diagrams had indicated that gas oil had been used as a raw charging stock, but to-day, as far as his knowledge went, the world was very short of gas oil, and he wondered how far the cracking of the heavier oils or the substances of which there was a surplus, such as bitumen, had been developed.   It seemed to him that there would have to be a move in the commercial world in that connexion, and that all the members must keep their minds open on the commercial side in the future, especially now that coal was becoming harder to obtain.   He did not think that the extensive cracking of gas oil could continue, and he would therefore like to know how far down the scale fluid catalytic cracking was likely to go.

The author had mentioned that some of the fluid catalytic crackers had not any heaters, and he would like to know what started them off.

DR. WALTER stated that the units referred to were warmed up by the air-heater and brought to operating temperature by burning oil in the regenerator.

The charging of heavy distillates to fluid catalytic cracking units had been demonstrated as a quite practical operation in a number of units operated during the war.   Also, one refiner had recently charged topped crude to a fluid-catalytic cracking unit for a period of a month.*   There are two factors which must be considered in topped crude operation : salt content and content of asphaltic materials in the topped crude.   Large quantities of asphaltic materials lead to high ·production of catalyst coke, which is expensive to burn.   Large quantities of salt will usually be harmful to catalyst activity.   He would therefore say that, at any rate at the present time, there were·two characteristics which a heavy oil must have if it was to be charged economically.   One was that the salt content must be low, and the other was that the content of coke-forming materials must be reasonable.   The meaning of " reasonable " would have to be determined according to the situation in each case.

DR. D. A. HOWES said that the process described by the author had been of tremendous importance during the war years, particularly in America, for three reasons.   First, it provided a means whereby aviation base stock could be made from a very wide range of crude oils, which had not been possible before.   Secondly, it enabled enormous quantities of butane to be produced for the alkylation process.   Thirdly, it enabled large quantities of butadiene to be made for synthetic rubber production.   He thought that the process was perhaps the largest single factor contributing to the enormous production of aviation gasoline in the United States during the war years.   He would go further than that, and say that the confidence placed

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* Since his return to the United States the author has learned of two other refiners who have been charging topped crude to their fluid units, both for periods of about four months.   These topped crude operations have been deemed successful and are being continued.

in catalytic cracking at the time when America came into the war had been of tremendous importance, inasmuch as the whole experiment had been a colossal success, and it had been the biggest single factor in the final air war against Germany. In fact, it was one of the greatest achievements in the petroleum industry in modern times.

All the members would agree that catalysts had come to stay in the petroleum industry and had a great future, but he did not think that the catalytic cracking process of to-day should be regarded as anything more than the first step in the development of what he liked to think of as a truly catalytic cracking process. The fluid unit, despite its great achievements and its great possibilities, was in its present form because the cracking process was still very largely uncontrolled, in the sense that the reaction produced carbon, which was deposited on the catalyst, and then had to be burned off the catalyst, which was used over again. Surely it would be desirable to have a catalyst which would effect the splitting reaction in such a temperature range that no coke was produced. Coke was not an essential in the reaction. Its production was an undesirable occurrence, and what was desired in the industry was a catalytic cracking process which did not produce coke. Such a process was not impossible theoretically, and it should not be impossible practically. An enormous amount of work would probably have to be done before it was devised, and that applied also to cyclization processes, which had the same disadvantage.

Without wishing to belittle the merits of catalytic cracking in any way, he thought it was right that certain disadvantages of the process should be pointed out.

The author had shown figures for the yields obtained from a gas oil, and it had already been mentioned that gas oil was in short supply to-day, and that attention should be given to the processing of heavier stocks. The author's figures showed that from gas oil there could be produced about 50 per cent of gasoline of 80 octane, about 35 per cent of cycle stock and about 15 per cent of gas. In the case of a very large number of crudes available in the world, the gas oil stock would have a cetane number of about 40. It was a very usable compression ignition fuel. The thermal efficiencies of the two engines, the compression ignition engine and the spark ignition engine, were approximately the same, so that what had actually been done was to lose 50 per cent of the original calorific value of the fuel. The 35 per cent of cycle stock, as could be seen by doing a very rough hydrogen balance in one's mind, must be very deficient in hydrogen compared with the starting stock and have a cetane number of about 10 or 20; in other words, it would be a quite unusable high-speed diesel fuel.

There was also a great disadvantage associated with the gas formation. He knew that it was a very valuable source of materials in war-time, from which alkylates and chemicals could be produced, but in a peace-time economy those synthetic materials would not be required to the same extent, and that applied particularly to the case of chemicals. A very few catalytic cracking plants would supply the world's consumption of those materials, and a considerable amount of the gas would then be wasted.

He therefore thought it was essential that the process should be applied to heavier stocks, but it had not yet been demonstrated that the process

was 100 per cent satisfactory on heavy wax-bearing stocks, and particularly upon asphaltic materials.

He would not like to give the impression that he did not appreciate the work which had been done on the process. A great deal of credit was due to the engineering skill that had been applied to the development of the process, and much credit was also due to the chemists who had been in the background, but he suggested that the present process should not be regarded as the final word in the matter. It was only a small beginning in the application of catalysts in a very broad way in the industry.

He would like to know whether the author could give any figure for catalyst losses in fluid catalysts plants. One would naturally expect the catalysts to lose its activity in use, and that might necessitate a certain catalyst replacement. There was also the question of mechanical removal of catalyst from the unit by way of fines. He would like to have some typical figures for these actual losses.

DR. WALTER said that the actual losses which had been encountered during war-time operation, with the use of the ground silica-alumina catalyst, had varied very widely from one operator to another. After things had settled down, however, and experience had been gained, it had appeared that with careful operation the catalyst loss would be about 0·3 lb per barrel. In discussing the relative importance of unavoidable losses and the replacement of the catalyst for the sake of maintaining its activity, one entered upon a complex field, and it must be admitted that it was a field which had not yet been sufficiently explored to enable an operator to determine exactly the activity level at which he should maintain his catalyst. He thought that, with one or two exceptions, up to the present time the catalyst replacement rates had been largely set by the mechanical loss.

DR. HOWES said that, on the basis of the author's figure of 0·3 lb per barrel, the loss would be $1\frac{1}{2}$ to 2 tons per day from a 10,000-barrel per day unit.

DR. WALTER agreed.

MR. C. S. WINDEBANK said that after the rather pessimistic note which Dr. Howes had just sounded, he would like to make a more optimistic comment about the potentialities of the fluid catalyst process, and draw attention to the fact that, apart from the cracking of petroleum, the fluid process presented an entirely new process technique which had possibilities in all branches of industry. Even though, as Dr. Howes had stated, the fluid catalyst process may have only scratched the surface of the problem of cracking, the principles on which it is based may in the future be used beneficially in many other branches of industry.

He wished to ask Dr. Walter a question regarding the cycle stock derived from the fluid catalyst process. This was aromatic in character and of poor quality as a diesel fuel, but in America it had a large market as heating oil. In Britain there was no such market for the material, and he would like to know whether the author could make any suggestions about the way in

which the balance of refinery operations could be modified to absorb such stock.

Dr. WALTER said that under such circumstances the catalytic cycle stock would presumably be thermally cracked to produce motor gasoline, with gas and heavy fuel oil as by-products.

He thought it would be found in most circumstances that it was not economic to crack catalytically a gas oil very severely for the production of motor fuel, but that it was better to crack it to a medium level and then take the cycle stock and crack it thermally.

Mr. C. I. KELLY said he wished to ask a question arising from Dr. Howes' contribution to the discussion and referring to the controllability of the fluïd cracking process. Was it possible so to control the operation that one could crack catalytically a good diesel oil with a high pour point on account of its wax content, and arrive at a finished material with a pour point well below zero and with a cetane number which has not been very adversely affected ?

There was another question about Table I, in which the author gave figures for what he called a natural catalyst and for silica alumina. He would like to have some more details about the natural catalyst. For instance, was it activated ?

Dr. WALTER, in reply to Mr. Kelly's first question, said he did not think it was possible to control the process in such a way as to give the result stated by Mr. Kelly. He thought that if the oil was cracked hard enough to produce a pour point well below zero, the cetane number would be quite markedly reduced.

Mr. KELLY asked whether the result to which he had referred had been achieved in America.

Dr. WALTER said that cycle stocks had been-used for diesel oil in America. He thought that he ought to stress the fact that the quality of the catalytic cycle stock would depend on the severity of the cracking operation. If the cracking conditions were mild—if, for example, only 35 per cent of the gas oil was cracked—the quality of the cycle stock approached that of the charge stock. If, on the other hand, the cracking conditions were severe and 70 per cent of the charge stock was destroyed, the cycle stock would become highly aromatic and have a low pour point, and would differ very considerably from the charge stock. At least one refiner whom he knew in the United States had carried out a catalytic cracking operation in which he cracked the oil relatively lightly and sold the lighter part of the catalytic cycle stock as diesel oil. He might have blended it a little, but he thought that the diesel oil contained a very large percentage of catalytic cycle stock. The term " cycle stock " could cover a multitude of specifications, even amongst the results from the same charge stock.

The natural catalyst to which he had referred was a natural clay which was activated. He was not familiar with the actual process of activation, but the clay was treated in some way to increase its activity.

MR. F. MACKLEY said he could not lay claim to be at all knowledgeable on the subject of fluid catalytic cracking, but in a recent tour of certain refineries in the United States he had become very conscious of a considerable amount of argument between the thermal crackers and the fluid catalytic crackers. In fact, he thought it might be said that there was a very definite division of opinion, particularly with regard to the economics of the two systems of cracking, and, so far as he had been able to gather, the advantages of fluid catalytic cracking had been largely dependent on its utility as a war-time measure. He would like the author to give his opinion on the economics of the fluid process as compared with those of the thermal process.

It had occurred to him that a quite large factor in the economics of the fluid catalytic process was the loss of catalyst to which reference had been made. As the catalyst/oil ratio might be between 15 to 1 and 20 to 1 (he thought that was about the normal figure with the natural catalyst), it could readily be appreciated that the fine powder was being circulated at such a terrific rate that there was a very considerable loss. Arising out of that and Dr. Walter's remarks on the development of the microspherical catalyst, he would like to ask whether the quality of a catalyst was dependent on some chemical characteristic, such as the silica proportion, or whether it depended on the free surface area or the available surface area of the catalyst itself. He believed that the natural catalyst when new had a surface area of about 500 sq. m. per gram, and that very shortly after use the surface area fell to about 200 or 300 sq. m. per gram. Did the introduction of microspherical catalyst such as the author had described reduce or increase the surface area, and, in so far as it might be possible to do so, did it reduce the catalyst/oil ratio?

There was one further point on which he would like to have the author's opinion. The statement was made in the paper that there were one or two plants which operated slightly above atmospheric pressure. Did the author think there was any possibility of developing the fluid catalytic process at higher pressures, thus reducing the catalyst/oil ratio and generally affecting the economy and the flexibility of the process?

DR. WALTER, in reply to Mr. Mackley, said that catalytic cracking was more expensive than thermal cracking. Higher liquid recoveries are obtained by catalytic cracking, but at constant gasoline prices the increased liquid recovery would not normally pay the increased costs. The important factor, however, was that catalytically cracked gasoline has a considerably better octane number than thermally cracked gasoline, and it was this improvement in quality which had brought about the current importance of catalytic cracking in the U.S. refining for civilian products.

The internal surface of a catalyst was related to its activity. This did not mean, however, that one could plot data on internal surface area versus activity for silica-magnesia, natural and silica alumina catalysts and obtain a single curve. Although surface area was a very important factor in catalyst activity, there were other factors which influenced it. As to whether silica was more important than alumina or *vice versa*, or whether silica was more important than magnesia or *vice versa*, it was impossible to say. In order to obtain effective catalysts it had been

found necessary to have both silica and magnesia or alumina in their compositions.

The catalyst/oil ratio was largely determined by the amount of heat liberation in the regenerator. In a fluid unit, particularly one where there was no furnace and no cooling mechanism on the regenerator, the heat of combustion of the catalyst was removed almost entirely as sensible heat in the catalyst. Therefore the rate of catalyst flow from the regenerator was controlled by the heat liberation, or in turn by the coke production. The coke production was determined by a number of factors, such as the type of charge and the severity of cracking, but under given conditions of operation was not radically affected by the type of catalyst; therefore it could not be said that one catalyst required markedly different catalyst/oil ratio than another.

The simplified unit which he had described operated under pressure on the regenerator. The regenerator pressure would probably be about 20 lb. There were difficulties in operating a catalytic cracking unit at high pressure, because raising the pressure increases the coke laid down. It was possible to increase reactor pressure somewhat above that generally used, but, after a number of analyses, he thought it was fairly generally agreed that there was no net advantage in markedly increasing the reactor pressure.

Mr. C. I. KELLY asked whether the author could give any comparative figures of the life of the three catalysts that he had mentioned, in terms of so many thousand gallons per ton of each catalyst irretrievably consumed.

Also, was it a fact that the capacity for cracking in the United States was now 60 per cent fluid catalytic and 40 per cent thermal? If that was the case, and if there was the indicated demand for large quantities of catalysts, did the refiners have to make their own catalysts?

Dr. WALTER said he did not think that the fluid catalytic cracking capacity in the United States was equal to anything like 60 per cent of the total cracking capacity in that country. About a year ago the capacity of the catalytic cracking units in operation in the United States was about 1,000,000 barrels per day, which would be about 150,000 tons.

With regard to the relative lives of the natural catalyst, the silica–alumina catalyst and the silica–magnesia catalyst, the natural catalyst was most susceptible to loss of activity. The lives of the other two were much the same, in terms of activity decline at a given temperature for a certain length of time. Catalyst activity was influenced to a considerable extent by the way in which the plant was operated. If the regenerator temperature was maintained at a high level, the catalyst would depreciate rapidly, whereas if the regenerator temperature was kept at a low level the catalyst would tend to lose its activity less rapidly. The optimum reactor temperature became a matter of economics, because it was more expensive, in terms other than catalyst consumption, to operate a cracking unit with a low regenerator temperature than it was to operate a cracking unit with a high regenerator temperature.

Mr. J. W. HYDE said he would like to ask a question concerning the precise physical state of the vapours at the reactor cyclone. Were the

vapours 100 per cent vapours or was there any liquid polymer which was unvaporized and hence would be removed by the cyclone and dropped back into the reactor ?

DR. WALTER replied that any liquid polymer which was unvaporized would show up as coke on the catalyst. Since it was his recollection that the coke content of the catalyst separated in the cyclone was not appreciably above that for the main body of catalyst, it would not seem that the phenomenon described by Mr. Hyde took place to any major degree.

MR. F. MAYO said that reference had been made to the difficulty of disposing of the cycle oil in the catalytic process, and he would like to ask whether it was not possible to crack to ultimate yield of gasoline. Must a cycle oil be taken out from the catalytic process ?
The author had referred to the U.O.P. once-through process, and had said that a heater was not necessary with that process, but that when re-cycling was adopted a heater was necessary. He would like to ask the author why a heater was necessary when recycling was adopted.

DR. WALTER said that the reason why one would not ordinarily crack to ultimate yields on a fluid catalytic cracking unit, or any other catalytic cracking unit, was that a point was reached (at perhaps 70 to 80 per cent oil destruction) where the yield of gasoline from the destruction of an additional barrel of cycle stock became uneconomically low; in other words, a large part of the additional oil destroyed went to gas and coke. That meant that an uneconomic level of cracking had been reached. The economic cracking level would vary from one plant to another, depending on local circumstances. He did not think there was any question that, for maximum gasoline yield, the conversion should be in the range 55 to 65 per cent and the cycle oil should be subjected to thermal cracking.
The reason why a heater was necessary in the re-cycling operation when it was not required for once-through operation was that when re-cycling was practised, the amount of oil, and therefore the amount of heat required to vaporize the oil and bring it to reactor temperature, was increased. On the other hand, at a given conversion level and temperature the coke production (in terms of pounds per hour), and therefore the heat of re-generation, for recycling operation, was slightly less than for once-through operations. Thus, if the heat of regeneration just about balanced the heat required to heat the reactor charge in once-through operation, it became necessary to supply heat from an external source—usually a heater—when recycling was practised.

MR. P. DOCKSEY asked whether proportionately less coke was made from the cycle oil when recycling was carried out.

DR. WALTER replied that he would not say that was the case but the coke production was slightly reduced at a given conversion level.

MR. P. DOCKSEY said he understood from the remarks made in the discussion that the heater would be needed if part of the feed was replaced

by a considerable amount of recycle oil, and he drew the inference that
the balance between the amount of heat obtained by burning the coke and
the amount needed to vaporize the oil was disturbed.   In other words, he
drew the inference that less coke was made.

DR. WALTER replied that slightly less coke was made, but to all intents
and purposes it could be said that the amount of coke made was the same.
Even if it was the same, however, the recycling operation made it necessary
to introduce heat from some extraneous source, because the heat load for
vaporizing the oil charged to the reactor was very considerably increased
and there was no longer sufficient heat of regeneration to vaporize all the
oil supplied to the reactor.

MR. DOCKSEY said his point had reference to coke on the combined feed.

DR. WALTER said that the coke on a combined feed would be considerably
reduced ; it would be reduced roughly in proportion to the combined feed.

MR. DOCKSEY suggested that that would be an important point if coke
production was a limitation.

DR. WALTER agreed.   If the once-through catalytic cracking process
was carried out, making 5,000 lb of coke per hour, and then recycling was
done, with the same fresh feed rate and at the same conversion level, other
conditions being constant, the absolute rate of coke production fell some-
what.   At the same time the heat requirement for vaporizing the oil
increased.

DR. HOWES asked whether in the cracking operation heavy oil was
produced which would not be vaporized if a furnace was not used.

DR. WALTER said that the mechanism of vaporization in the presence of a
catalyst was rather difficult to follow, but if any heavy oil remained un-
vaporized it would appear as catalyst coke.   That, presumably, was one
of the main reasons for high coke production from very heavy oils.

MR. MAYO asked whether, when recycling was carried out, the ratio of
catalyst to total feed was reduced.

DR. WALTER said that if the small reduction in the number of pounds of
coke produced per hour were disregarded, and it was assumed that coke
production remained constant, then the heat of regeneration would be un-
changed, and the rate of catalyst flow from the regenerator to the reactor
feed line would be the same as for once-through operation for a given amount
of fresh feed.   Thus the ratio of catalyst to total feed would be lower for
recycle operation than for once-through operation.

DR. A. W. PEARCE, referring to the question of the materials of which the
feed unit was constructed, asked whether extensive use was made of alloy
steels.

A A

With regard to the use of heavier stocks for cracking, he noticed that the Thermofor catalytic process had been adopted for use with reduced crudes. If that was so it seemed reasonable to assume that the process could be used for similar charge stocks.

On the question of diesel oils, an article had been published on cycle stocks from catalytic cracking in which it was mentioned that the cetane number of the cycle oil was between 39 and 41. It therefore seemed quite possible that the fluid catalytic cracking process could be used to produce cycle stocks with similar cetane numbers.

DR. WALTER said that for low sulphur stocks the unit was made of carbon steel. The regenerator was fitted with a monolithic lining which was supported on a grating structure. For high sulphur stocks the reactor and at least a section of the fractionating column was lined with alloy steel.

The liquid catalytic cracking of heavy oils had been carried out commercially for a period of about a month in a full-scale 15,000-barrel commercial unit. In any catalytic cracking process, however, there were the two drawbacks which he had already mentioned—namely, that if the stock contained large quantities of asphaltic materials the coke production would be high, and that if the salt content of the stock was high the rate of catalyst deterioration would be a serious factor.

With regard to the production of diesel oil with a 40 cetane number, the refinery which he had mentioned had produced diesel oil with a 40 cetane number from almost entirely catalytic cycle stock. It was largely a matter of how severely the oil was cracked. If it was cracked lightly and the cetane number of the charge was high, the cetane number of the cycle stock would be high. If the oil was cracked severely, the cetane number of the cycle stock would be low relatively to the cetane number of the charge stock.

THE CHAIRMAN said that the trend in the aviation world, where jet turbine propulsion was replacing the piston-type engine with the alteration in fuel requirements, was one of the many changes which must be watched by refiners when selecting plants, and whilst a catalytic cracker was an excellent tool to give flexibility in product manufacture from almost any raw stock, and as such would hold its place in most of the larger refineries, it must be remembered that there were many small refineries which could not afford such a high capital expenditure as was called for by this type of equipment.

On the motion of the Chairman, a vote of thanks was accorded to Dr. Walter, and the meeting then terminated.

THE DEVELOPMENT OF IMPROVED TURBINE OILS.

By C. N. Smith * and G. H. S. Snyder.*

Introduction.

The mounting demand for high-quality steam-turbine oils and the increasing use and successful application of inhibited oils have made the development of improved turbine oils of growing interest to the turbine operators and builders, as well as to the refiner.

Under average service conditions, high-quality, straight mineral turbine oils properly refined from selected crudes adequately meet the lubrication requirements of most steam turbines. Premium-quality straight mineral oils have given satisfactory service over periods as long as twenty-five years, and service periods of ten years under average operating conditions are quite common. However, in spite of careful crude selection and refining to obtain optimum quality, the more severe operating conditions encountered in some turbine installations have made it necessary to develop additive type oils having oxidation resistance characteristics and rust-preventive properties not attainable with straight mineral oils. It has always been recognized that some turbines impose more severe service conditions on the lubricating oils than other turbines, even though the so-called " severe turbines " have essentially the same design as " normal turbines." Such conditions have usually been the result of certain operating and maintenance features or the presence of contaminants which are difficult to avoid or eliminate from turbine systems. The trend towards larger power installations operating at higher temperatures has occasionally resulted in more rapid oxidation of straight mineral oils. Also, particularly during the war years, turbines have been subjected to longer continuous service under greater loads than are normally experienced. Therefore, oxidation-inhibited oils were introduced to provide greater oxidation stability under those service conditions where straight mineral oils were found inadequate.

The introduction of oxidation-inhibited oils influenced to some extent the demand for rust-inhibited oils. Experience had shown that with straight mineral oils the normal oxidation products sometimes had the very useful property of inhibiting rusting caused by frequently unavoidable water contamination. But the use of oxidation inhibitors prevented the formation of such rust-inhibiting oxidation products. However, the effect of even small quantities of oxidized oil in decreasing the effectiveness of oxidation inhibitors prevented the addition of oxidized oils to oxidation inhibited oils or the use of oxidized oils for " seasoning " of metal surfaces in the turbines.

With the advent of the war, and the consequently accelerated production, abnormal contaminants sometimes caused greater oil deterioration and

* Socony-Vacuum Laboratories (A Division of Socony-Vacuum Oil Co., Inc.) Research and Development Department, Paulsboro, N.J.

operational difficulties than would normally have been encountered, or which during peace-time could have been more easily corrected. Serious rusting experienced in marine service focused considerable attention on the desirability of using rust-inhibited turbine oils, inasmuch as time, facilities, and trained personnel were not available to correct the widespread rusting encountered.

Therefore, it may be said that the need for improved turbine oils, and particularly inhibited turbine oils, is a natural outgrowth of the inherent limitations of even the highest-quality straight mineral oils in meeting the requirements of some severe turbines. In view of the successful application of and the growing interest in inhibited turbine oils, it is felt that a general discussion of some typical methods of evaluation of inhibited turbine oils would be in order.

DEVELOPMENT AND EVALUATION OF TURBINE OILS.

The evaluation of turbine oils requires a great amount of time in the performance of both laboratory tests and field tests under actual service conditions. With straight mineral oils the problem is somewhat simplified by the fact that laboratory tests may be readily accelerated and, generally speaking, fairly good correlation can be obtained between such laboratory tests and average service conditions. With inhibited turbine oils the problem is complicated by the fact that even with greatly accelerated laboratory tests many months may be required for the evaluation of new product formulations, and the interpretation of such evaluations is particularly difficult because of the lack of sufficiently accurate correlation between laboratory tests and field performance with additive type oils.

Some of the most important factors to be considered in the evaluation of inhibited turbine oils may be outlined as follows :

(1) *Good Base Oil Stability.*—The mineral-oil base must be a good turbine oil, even without the addition of oxidation inhibitors. The base oil should have a slow rate of oxidation, so that in the event of depletion or exhaustion of the oxidation inhibitor the subsequent rate of oxidation shall be slow enough to enable the operator to detect over a period of months the deterioration of the oil, in order to arrange for installation of a new charge of oil before the danger of high acidity, sludge formation or viscosity increase interferes with the turbine operation.

(2) *Inhibitor Response.*—The mineral-oil base should have good response to the action of suitable oxidation inhibitors in order to provide as much resistance to oxidation as possible under the severe oxidizing conditions for which such oils are intended.

(3) *Additive Compatibility and Activity.*—The additives used should be compatible with the oil under all normal conditions of service and storage. They should not by reason of chemical reaction cause the formation of deposits or metal soaps, or corrode the metal surfaces in the system. They should not be water soluble, in order to avoid depletion by washing action of the water which is present to some extent in turbines. And of course the additives should have no deleterious effects on normal physical characteristics such as demulsibility in service.

Any complete programme for the development or improvement of inhibited turbine oils requires the evaluation of stocks from many possible crude sources, methods and degrees of refining, and different types and concentrations of inhibitors.

While there are many tests which are designed to determine the relative oxidation stability of turbine oils, they do not necessarily provide this information, because of certain limitations of the various procedures. For example, some such tests provide for the determination of oil deterioration after fixed periods of oxidation, and others provide for the determination of only the induction period, while some determine, in addition to induction period, the rate of oxidation after the induction period. Any oxidation test, to be of real value, should correlate with field service and arrange the oils in the same order of merit as turbines in the field.

OXIDATION TESTS.

To illustrate some of the various types of oxidation tests, let us consider two which are undoubtedly known to all who are familiar with turbine testing—the Brown Boveri * and the A.S.T.M. Turbine-Oil Oxidation Test †—and one developed in the Socony-Vacuum Laboratories, and known as the " Simulated Field Service Test for Turbine Oils," hereinafter referred to as S.F.S.Test.

(1) *Brown Boveri Turbine-Oil Oxidation Test.*—This test illustrates the simplest type of accelerated laboratory oxidation test. It is a " beaker test " in which a 200-ml sample of oil is maintained at a temperature of 110° C (230° F) for 72 hours in the presence of a 70 mm × 40 mm × 1 mm strip of copper as catalyst. Air moving slowly over the surface of the oil provides oxygen. There is no agitation or stirring of the oil. After the 72-hour ageing period the extent of oil deterioration is determined by measurements of acidity, colour, sludge, or viscosity as desired.

(2) *A.S.T.M. Turbine-Oil Oxidation Test.*—In this test a 300-ml sample of oil contained in a large " test-tube " is oxidized at a temperature of 95° C (203° F) in the presence of 3 metres each of iron and copper wire (No. 14 A.W.G.) and 60 ml of distilled water, with pure oxygen bubbled through the oil at a rate of 3 litres per hour. A water-cooled condenser serves to maintain the water in the test, and retains any volatile oxidation products that would otherwise escape. The test is continued until the oil has attained a neutralization value equivalent to 2·0 mg KOH, and may require from less than 100 hours to more than a year to complete, depending on the stability of the oil.

(3) *S.F.S.T.*—This is a more elaborate test than either of the others described. In this procedure a six-litre sample of oil in a glass reservoir (see Fig. 1) is circulated through 5 ft of ⅜-in copper tubing by a pump outside the reservoir. In addition to the copper tubing, 300 sq. in. (total surface) of Admiralty metal and 98 ft of No. 18 A.W.G. iron wire are placed in the reservoir as catalyst and 200 ml of distilled water are added daily.

Oxygen is supplied by the air, which is drawn into and intimately mixed with the oil by the rapidly rotating spindle, which is supported by a Babbitt bearing below the oil level. The oil is maintained at 198° F by an immersion heater. The test is continued until the desired degree of deterioration has been produced, as determined by measurements of acidity, viscosity and colour change, and sludge formation, and may require from several days to more than a year to complete a test, depending on the quality of the oil and whether or not it is inhibited.

While there are many laboratory oxidation tests for turbine oils, these three represent the general types, and serve to illustrate some of the advantages and disadvantages of such tests.

The Brown Boveri test shows the deterioration of an oil after an arbitrarily chosen period of time, but does not reveal the progressive deterioration of the oil. It shows relative differences in acid formation by oils of poor quality as compared with both inhibited and uninhibited oils of high quality, but fails to differentiate between various high-quality straight mineral oils or inhibited oils. Because of the limited severity of this test, successfully inhibited oils show no acid formation, and high-quality straight mineral oils may show neutralization values of as low as 0·05, which is little greater than the limit of experimental error in determining acidity. Thus, high-quality oils which may have greatly different service lives may display the same stability in this test.

The life of an oil in the A.S.T.M. Turbine Oil Oxidation test is defined as the time required to reach a neutralization value of 2·0. This test is so highly catalyzed that even very high-quality straight mineral oils will begin to show acidity in about 50–75 hours, and then oxidize so rapidly in the next 25–50 hours that a neutralization value of 2·0 or more is reached.

The differences in the test life of various straight mineral oils are generally within the limits of reproducibility; therefore this test will not show the differences in quality of straight mineral oils which in service may actually show greatly different useful service periods. This test does provide a means for determining inhibitor potency and response of base stocks to various additives. But, as with straight mineral oils, as soon as measurable acidity develops, the ensuing rate of oxidation of inhibited oils is so rapid that the slight differences in the rate of acid build-up are of no practical significance. Therefore, while the test shows the relative inhibitor response of oils, it fails to distinguish between inhibited oils, which in service might have the same induction period but, because of differences in base stock stability, would show considerable differences in *useful* life. It is easy to formulate an oil which will show a long A.S.T.M. life and presumably a corresponding stability in service, but which, because of poor base-stock stability, would oxidize so rapidly after exhaustion of the oxidation inhibitor that it would be hazardous for turbine service.

It should also be pointed out that although successfully inhibited oils may have greater stability than straight mineral oils under certain severe service conditions, it should not be assumed that the service life will be directly proportional to the improvement indicated by the A.S.T.M. Test or any other laboratory test. A straight mineral oil having an A.S.T.M. life of 100 hours may have a normal service life of ten years. When suitably inhibited, this oil may have an A.S.T.M. life of 1000 hours, but this does not
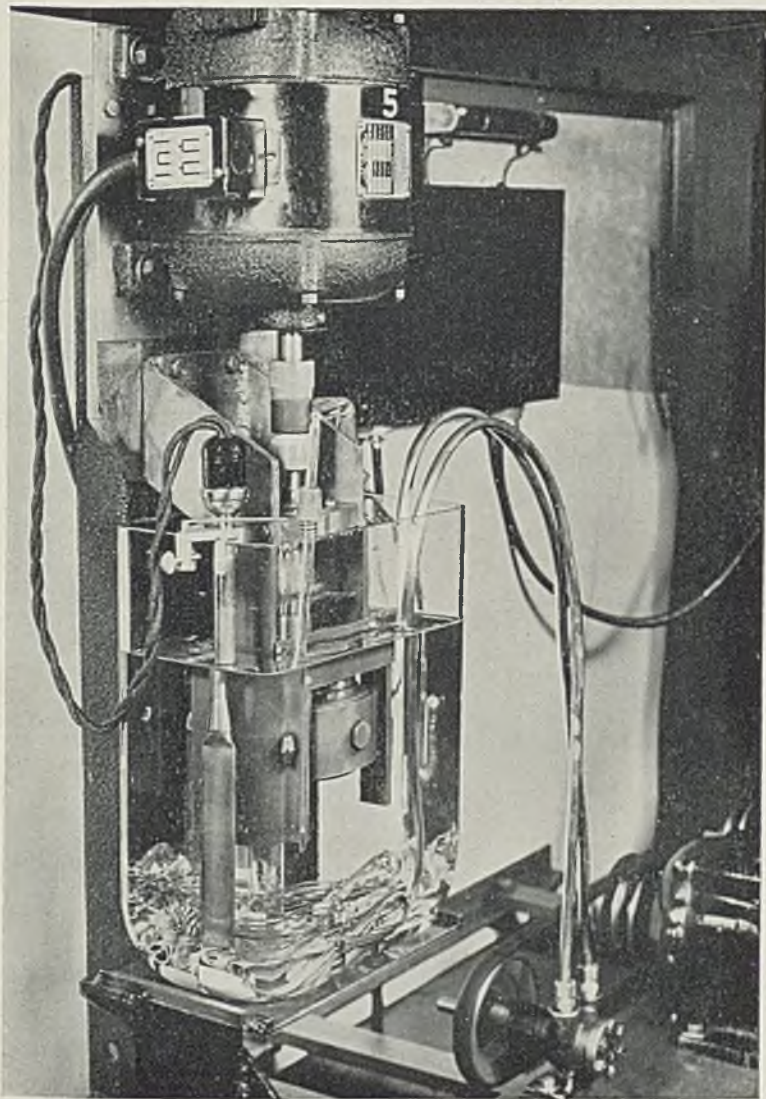
Fig. 1.

SIMULATED FIELD SERVICE TEST FOR TURBINE OILS (S.F.S.T.).

mean that the inhibited oil will then have a life of 100 years under the same service conditions as the uninhibited oil.

While the various laboratory turbine oil-oxidation tests will indicate the probability of greater service life for certain inhibited oils, none will predict the actual life of any oil under service conditions.   Because the service conditions and their effect on an oil vary from one unit to another, even in turbines of the same design, the results obtained in practice may be at variance with the results indicated by laboratory tests.

The Simulated Field Service test is applicable to the evaluation of both inhibited and uninhibited turbine oils.   The large amount of oil permits liberal sampling without appreciably changing the oil volume.   The conditions of oxidation are such that the rate of deterioration, as indicated by acid formation, viscosity change, and sludge formation, is relatively gradual as compared with the A.S.T.M. test and similar procedures, making it possible more clearly to differentiate between various oils.   As will be further illustrated, this test shows differences in the induction period * and the subsequent oxidation of either straight mineral oils or inhibited turbine oils, arranging the oils in the same order of merit indicated by field tests.   The S.F.S. test shows approximately the same induction period as the A.S.T.M. test, but emphasizes the differences in the ensuing rate of acid build-up (see Fig. 2).

Rust Tests.

For the evaluation of rust-inhibiting characteristics there is one generally used and accepted test—A.S.T.M. D665-44T.   There are several other rust tests, but none has had as wide acceptance as the A.S.T.M. procedure.

In this A.S.T.M. Rust test a polished steel rod is suspended in the oil at 140° F and 10 per cent by volume of distilled water (synthetic sea-water solution for marine turbine oils) is added to the oil.   The oil-and-water solution is stirred for 48 hours, after which the specimen is examined for the presence of rust.   Such a test will show the relative ability of different oils to inhibit rusting under these arbitrary conditions, but it does not necessarily indicate probable performance characteristics.

While this test has undoubtedly been of considerable help in the laboratory development of rust-inhibited turbine oils, hundreds of tests on samples taken from many turbines in the field show that the test does not indicate the actual ability of the oil to protect against rusting in service. · Many such oils which do not pass the A.S.T.M. Rust test are in service in turbines which are operating under wet conditions with no evidence of rust.   In the case of used uninhibited oils this indicates that this test is too severe, while with used inhibited oils it undoubtedly indicates inhibitor depletion or adsorption of the inhibitor on the metal surfaces.

This test does not show any chemical activity which a rust inhibitor may exhibit with other metals present in turbine systems, such as copper or copper alloys, but serves only to show relative ability in preventing rusting under these particular test conditions and is therefore indicative only of possible rust-inhibiting ability.

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* Induction period, for the purpose of this discussion, is arbitrarily defined as that time for measurable acidity to develop in the tests described.

UTILIZATION AND INTERPRETATION.

To illustrate the use of these various tests in experimental turbine oil development, consider first the data in Table I and Figs. 2, 3, and 4. In Table I are given the neutralization values from Brown Boveri tests of six

TABLE I.
Brown Boveri Oxidation Test.

				Oil A.	Oil B.	Oil C.
Neut. value, mg KOH per gm				1·0	0·25	0·08

	Oil A plus Inhibitor " X."	Oil B plus Inhibitor " X."	Oil B plus Inhibitor " Y."	Oil C plus Inhibitor " X."	Oil C plus Inhibitor " Y"
Neut. value, mg KOH per gm	0·02	0·02	0·02	0·02	0·02

oils. The relative stability of oils A, B, and C are roughly indicated by their neutralization values, but the other oils are shown to be the same.
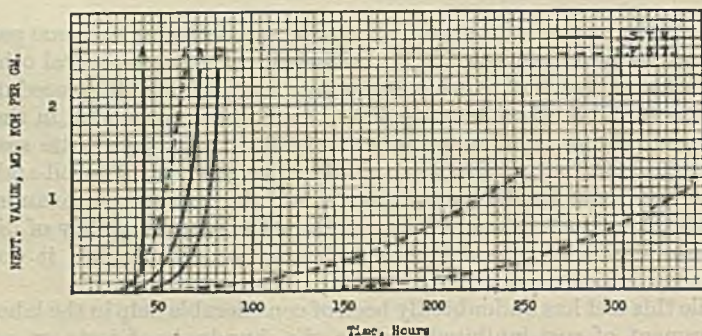

FIG. 2.

COMPARISON OF RATE OF ACID FORMATION OF DIFFERENT STRAIGHT MINERAL TURBINE OIL STOCKS BY THE A.S.T.M. TURBINE OIL OXIDATION TEST AND THE SIMULATED FIELD SERVICE TEST.

In Fig. 2 the A.S.T.M. Oxidation test data (solid lines) show oil A to be relatively poor, but do not show any appreciable difference between oils B and C. On the other hand, the S.F.S. test data in Fig. 2 (dotted lines) clearly show differences in not only the induction periods of oils A, B, and C, but also in their subsequent rates of oxidation.

The A.S.T.M. Oxidation test data in Fig. 3 show the relative response of oils A, B, and C to different inhibitors, but no differences in the rates of acid formation of the inhibited oils after induction. The combination of the S.F.S. and A.S.T.M. Oxidation tests results together clearly show both the relative base oil stability and the inhibitor response characteristics of these oils.

Oils B and C are both known to be excellent turbine oils from actual field experience under average conditions, having *relative* service lives approximately as indicated by the S.F.S. test data. When oxidation of either of these oils does start, the rate of acid build-up is very slow, requiring even in the *most severe* cases six months to a year to develop a neutralization number of from 1·0 to 2·0. Under average service conditions such oils last for years, without showing any appreciable deterioration. The A.S.T.M. Oxidation test data show that the oxidation stability of oils B and C can be considerably improved by the use of suitable inhibitors, and the base-stock characteristics, as established by the S.F.S. test and field experience, are assurance that such inhibited oils would not oxidize
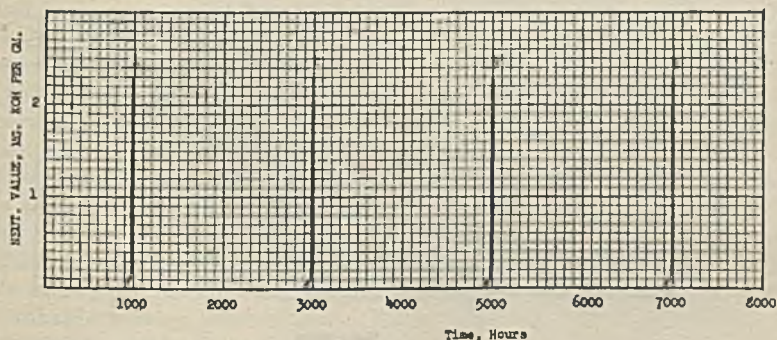

FIG. 3.

DETERMINATION OF INHIBITOR RESPONSE OF DIFFERENT TURBINE OIL STOCKS BY THE A.S.T.M. TURBINE OIL OXIDATION TEST.

1. Oil C plus Inhibitor " X " and Oil C plus Inhibitor " Y."
2. Oil B plus Inhibitor " X."
3. Oil B plus Inhibitor " Y."
4. Oil A plus Inhibitor " X."

at an excessive rate in the event of inhibitor depletion or exhaustion. On the other hand, the A.S.T.M. test indicates that oil A has much greater inhibitor response than either B or C, but the S.F.S. test shows that the rate of oxidation of this oil is so rapid that in the event of inhibitor exhaustion in service, this oil might deteriorate so rapidly as to result in serious mechanical failure. Oils of this type are therefore to be considered hazardous for use in turbines.

It is interesting to note that the induction period of an inhibited oil is approximately the same in the A.S.T.M. Oxidation test and S.F.S. test. This is illustrated by Fig. 4. While the induction period of this oil is shown to be almost exactly the same by either test, the induction period obtained on the S.F.S. test is sometimes slightly longer than by the A.S.T.M. Oxidation test. The important point is that the S.F.S. test oxidation curve shows the oxidation rate of the mineral-oil base of an inhibited oil as well as the induction period, and will therefore emphasize the differences in oxidation characteristics of various inhibited oils. The rate of acid formation has been used to illustrate how each of these tests may be used to evaluate turbine oil-stability characteristics, because determinations of

acidity indicate most readily the extent of oxidation. In the S.F.S. test curves similar to those obtained for acid formation are also obtained for viscosity increase and colour change. Sludge-forming tendencies of different oils are indicated both by visual observations of the oil and catalyst and by measurements of the amount of sludge formed as the acidity of the oil increases.

In the laboratory the Brown Boveri test can be utilized as a rough screening test to determine what oils are worthy of complete evaluation by the S.F.S. and A.S.T.M. Oxidation tests. If Brown Boveri test results are of a high-quality level, straight mineral oils can be completely evaluated by the S.F.S. test, and then tested for inhibitor response by the A.S.T.M.
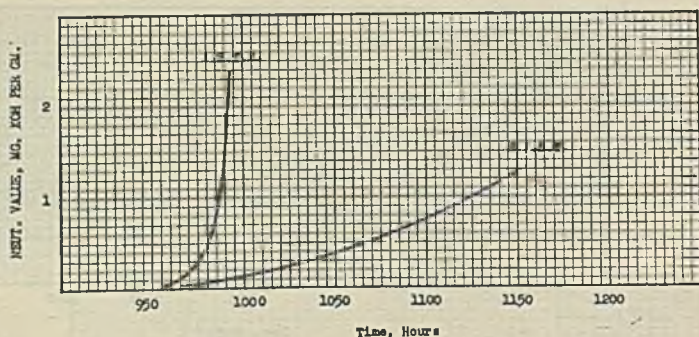

Fig. 4.

COMPARISON OF RATE OF OXIDATION OF INHIBITED TURBINE OIL (OIL C PLUS INHIBITOR " x ") BY THE A.S.T.M. OXIDATION TEST AND THE SIMULATED FIELD SERVICE TEST.

Oxidation test. If these tests are satisfactory, complete S.F.S. test data are obtained on the final inhibited formulations. New oxidation inhibitor possibilities are tested in various concentrations in different types of base stocks by the A.S.T.M. Oxidation test while the effect of different refining methods on a particular raw stock is evaluated by the S.F.S. test. Possible rust inhibitors are compared by the A.S.T.M. Rust test (D665-44T), but, as previously indicated, such tests are not necessarily indicative of service performance, and final selection of a rust inhibitor is dependent on the results of field tests under actual service conditions.

ADDITIVE COMPATIBILITY AND CHEMICAL ACTIVITY.

Additives should be evaluated not only for their effect on oxidation stability and rusting, but also other important service characteristics. Washing tests should be made on the oils to determine whether or not any appreciable amount of the additives may be removed by water contamination in service. Observations to determine whether or not the additives have any chemical effect that may cause metal corrosion or deposit formation should be made in both laboratory tests and field tests. While a test such as the Simulated Field Service test is well suited for making visual observations of corrosion or deposit-forming tendencies, like many other

highly catalyzed laboratory tests, it may fail to show some undesirable service characteristics. Because of the relatively high ratio of catalyst surface to oil volume in laboratory tests, the chemical attack of an additive may not show any appreciable effect, but in actual service, because of the very high ratio of oil to metal surface in the circulation system, the oil could cause an appreciable amount of corrosion of metal surfaces.

One of the most important characteristics of rust inhibitors to be determined is what effect they might have on demulsibility in service. Because such additives are highly surface active, they tend to decrease the demulsibility of mineral oils as determined by such conventional laboratory tests as the Steam Emulsion test, Herschel Demulsibility test, and other similar procedures. Similar to the rust tests, demulsibility tests have been of aid in developing inhibited oils, but none of them tells what an oil will actually do in service. For example, an oil which meets the arbitrarily prescribed Steam Emulsion requirements at the time of manufacture may show values 100 or 200 per cent higher after only a very short period of service, or even after a few months' storage, yet such oils have, from long experience, caused no difficulty in actual service.

Therefore, in summary, it should be recognized that satisfactory laboratory tests with regard to oxidation stability, rust inhibition, and demulsibility characteristics are not alone sufficient to justify marketing a new turbine oil, but together with the background of field experience, a complete knowledge of crude source and refining methods, are only indicative of probable service performance. Such tests are, however, suitable for determining what oils are satisfactory for further testing under actual field conditions, final evaluation depending on the results of such field tests.

FIELD TESTING OF TURBINE OILS.

Because of the many variables encountered in turbine operation, field testing of new turbine oils must be carefully planned. Mechanical changes, such as re-location or insulation of oil lines, installation of centrifuges for the removal of water, alteration of oil temperatures, or venting of a turbine, have considerable effect on the useful life of an oil, and it is therefore imperative to choose for field testing a turbine for which the complete service history is known. The oil temperatures throughout the system should be kept the same, in so far as possible, during field testing of an experimental oil. If in the past a turbine has operated under wet conditions, it should continue to operate in the same manner. Not only should such mechanical and physical details be known and reproduced, but, in order to make a significant evaluation of an experimental turbine oil, the unit selected for field testing should be one for which service history with several different types of oils is known. For example, in one unit, field tests have shown that a particular inhibited turbine oil will give a service life shown by both inhibited and uninhibited oils previously installed in this turbine, and this oil is still operating satisfactorily with little change.

Simply long life of an oil in a turbine is not necessarily indicative of outstanding performance characteristics. If a single turbine which imposes relatively mild operating conditions on the oil is chosen for field tests, an experimental oil may be made to appear to have better performance

characteristics than it will actually have in over-all average turbine service. Therefore, it is important to choose several different types of turbines for field tests in order to obtain representative service results. Carefully planned field tests will not only provide an actual evaluation of service life of an experimental oil, as compared with other products, but will disclose any faults that were not indicated by laboratory tests, with respect to oxidation stability, rust inhibition, demulsibility, and other performance characteristics.

THE INSTITUTE OF PETROLEUM.

Trinidad Branch.

The Eightieth General Meeting of the Trinidad Branch of the Institute of Petroleum was held at the United British Club, the Chair being taken by Dr. J. E. Smith.

The following paper was read :—

MINERAL OIL FILMS IN RELATION TO MOSQUITO CONTROL.

By A. Crossfield, B.Sc. (Associate Member), and G. F. Hazzard, B.Sc., A.R.C.S. (Member).

The control of mosquito larvæ by means of oil spraying has been practised for many years, but the application of fundamental principles to the manufacture of oils of suitable characteristics with respect to the formation of continuous mineral oil films on water surfaces is of quite recent origin. Lord [1] has described work carried out in Burma and Assam in which Adam's apparatus [2] was used to measure the ability of oils to spread on water surfaces. The present report covers work on a similar basis carried out in Trinidad, B.W.I., where mosquito-breeding conditions are somewhat different from those in Burma. It cannot be emphasised too strongly that although the appearance of malaria in man is very similar throughout the world, the conditions under which mosquitoes breed vary greatly, and methods of control must be adapted to the conditions of the locality. Throughout this report the references are solely to Southern Trinidad, but it is thought our deductions are sufficiently fundamental to be applicable to other areas, particularly as Lord in Burma obtained rather similar results.

In Trinidad, malaria is transmitted by *Anopheles aquasalis* and *Anopheles bellator*, the former breeding usually in stagnant, brackish water, of which there are large areas, the latter in the water collected by air plants (*Bromelliads*) growing in the forest trees. *Anopheles aquasalis* can be controlled by the spraying of larvicides on the breeding areas, but until recently *Anopheles bellator* could only be controlled by the removal of all trees harboring the *Bromelliads* in which the mosquito breeds or by the repeated removal of all the *Bromelliads*. Obviously this measure is practicable only in limited areas, but recent work by the U.S. Authorities and the Trinidad Government has demonstrated that effective control can be obtained by means of dilute copper sulphate solution applied from the ground by high-pressure sprays. Petroleum oils cannot be used in this manner in their present form because they would damage the foliage and the crops planted beneath the trees. Development of spraying methods with aeroplanes may one day make it possible to control *Anopheles bellator* by relatively inexpensive methods.

THEORETICAL CONSIDERATION OF SPREADING.

Adam [3] gives a comprehensive discussion of surface films of insoluble substances on liquids, and demonstrates how the phenomena may be visualized by means of molecular models based on the chemical formulæ of substances.

The conditions affecting the behaviour of an oil drop on water may be visualized by considering the surface forces acting on it, i.e., the interfacial tensions :—Tw/a water-air, To/a oil-air and To/w oil-water :
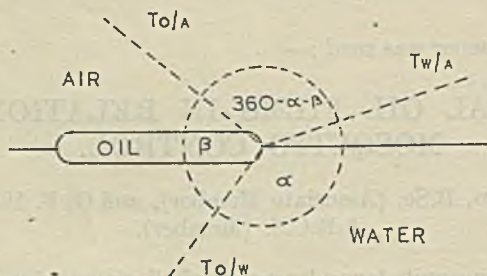
If the oil drop is in equilibrium, then the three interfacial tensions are in equilibrium, and the following relationship holds :—

$$\frac{Tw/a}{\text{Sin } \beta} = \frac{To/a}{\text{Sin } \alpha} = \frac{To/w}{\text{Sin } (360 - \alpha - \beta)}$$

The equilibrium of the oil drop on water can be disturbed by alteration of any one of the three tensions involved. In the case under consideration increase of the surface tension of the water Tw/a or decrease of the interfacial tension To/w will cause the angle β to decrease until it becomes zero. At this point the oil will spread if :

$$Tw/a > To/a + To/w$$

A measure of the ability to spread is obtained from the magnitude of the difference between these two factors :

$$Tw/a - To/a - To/w$$

which has been called the spreading coefficient [4] or the spreading pressure. The higher the spreading pressure of an oil the more readily it will spread on a contaminated surface.

In the practical application to mosquito control the surface tensions of the oil and water are fixed within rather narrow limits, and it is therefore necessary to reduce the interfacial tension. This modification can readily be obtained by the addition to the oil of oil-soluble polar compounds consisting of a long hydrocarbon hydrophobic group and a short hydrophilic group. Long-chain fatty acids, alcohols, and sulphonates are typical compounds which can be used.[5, 6, 7]

MEASUREMENT OF SPREADING PRESSURES.

Spreading pressures were determined as described by Lord [1] using the Adam Langmuir trough, the only modification being the use of oleyl

alcohol as the buffer film. The measurements were made at room temperature, 26° to 29° C, no allowance being made for this small temperature variation, which is not significant in this type of work.

SPREADING PRESSURES OF PETROLEUM FRACTIONS.

The spreading pressures of a number of typical refinery fractions were determined, and are recorded in Table I. In the case of fractions contain-

TABLE I.

Spreading Pressures of Refinery Fractions from Trinidad Crudes.

Oil.	Specific gravity at 60° F.	Distillation range, ° C.	Spreading pressure, dynes/cm.	
			Before soda wash.	After soda wash.
Kerosine	0·801	150–250	15·0	11·0
Kerosine Edeleanu extract .	0·867	150–250	—	8·3
Kerosine Edeleanu raffinate .	0·797	150–250	—	12·6
Gas oil	0·890	220–370	14·3	10·2
Gas oil	0·870	170–330	17·5	11·2
Gas oil Edeleanu raffinate .	0·809	220–370	—	4·3
Gas oil Edeleanu extract .	0·953	220–370	—	15·0
Lubricating oil distillate . .	0·920	250–over 400	14·0	7·7

ing naphthenic acids a marked reduction in spreading pressure is noticed on removal of these acids by soda-washing.

Table II shows the effect of adding various oil-soluble polar compounds

TABLE II.

Effect of Additive " A " on Spreading Pressure of Gas Oil.

Additive, % vol.	Spreading pressures, dynes/cm. at temperature 26° to 29° C.				
	Naphthenic acids,	Coconut oil fatty acids.	Oleic acid.	Additive A.	Additive T.
0	10·4	10·4	10·4	10·4	10·4
0·25	15·5	14·4	17·3	16·5	17·0
0·5	16·3	15·8	19·4	19·0	18·8
1·0	16·8	21·1	21·5	22·0	21·2
2·0	17·5	24·0	24·0	—	23·5
5·0	19·7	26·7	27·6	—	28·5
100·0	27·0	Over 30	Over 30	—	—

to a gas oil. Available fatty acids are too expensive for addition to anti-malarial oils, and therefore from petroleum two additives have been developed in addition to napthenic acids. They are referred to as additives " A " and " T " in the table.

The effect of a given quantity of polar additive is more marked with some

oils than with others, thus with Edeleanu extracts rich in aromatic fractions a smaller increase of spreading pressure is given than with the corresponding raffinates. A series of results using additive " T " are given in Table III to illustrate this effect. Similar results are obtained with other additives.

TABLE III.

Effect of Additive " T " on Spreading Pressures of Oils.

	Additive % vol.	Gas oil.	Gas oil extract.	Gas oil raffinate.	Kerosine extract.	Kerosine raffinate.
Specific gravity at 60/60° F.	—	0·845	0·953	0·829	0·867	0·797
Spreading pressures, dynes/cm, 26° to 29° C.	0	10·4	15·0	4·3	12·6	8·3
	0·25	18·0	17·0	18·8	25·3	23·0
	0·5	25·0	19·0	26·5	—	28·5
	1·0	—	23·0	—	—	28·5

TOXICITY TESTS.

In the initial experiments on toxicity of oils for mosquito larvæ, *Anopheles aquasalis* and *Culecine* larvæ from typical local breeding areas were used. For this series of tests the bowls were 9½-inch diameter enamelled steel, carefully cleaned with I.P. petroleum spirit to remove traces of oil from previous tests, and washed under a strong stream of water before filling by overflowing, and final adjustment of the water level ½ inch below the rim. From ten to twenty larvæ were placed in the bowl, and enough oil to give a film 10 microns thick was added. Observations of the number of larvæ oiled and unable to rise to the water surface were made, and in general complete kills were obtained in less than ½ hour, although oils varied in rapidity of kill.

The results obtained are summarized in Table IV. The toxicity is expressed as the mean time in minutes for all larvæ to fall and not subsequently rise, and in each case is based on a minimum of five tests. The latter part of the tabulation illustrates the results in a different manner. Based on the time for all larvæ to fall, the order of effectiveness of the oils has been given for each test, the mean deduced, and the oils arranged in decreasing order of toxicity from 1 to 9. This has the advantage of rating the oils in order of toxicity regardless of the variety of larvæ used for the individual tests, but has the disadvantage that oils with similar rapidity of kill may show widely varying order of toxicity. With these larvæ the times for killing are so short in comparison with the variations in individual tests that no reliable comparison of effectiveness of oils can be made.

Later the technique used by the London School of Hygiene and Tropical Medicine with larvæ of *Aedes ægyptii* (a species of the *Culex* type) was adopted with the following detailed procedure. Large porcelain basins about 30 cm diameter were carefully cleaned with chromic acid mixture and washed with distilled water. A cut-off bottle top cleaned in a similar manner was placed in each bowl so that the neck of about 1¼ inch diameter could be used for introduction and removal of the larvæ without passing them through the oil film. The bowls were filled with distilled water to

TABLE IV.

Toxicity Tests.

	Viscosity at 70° F, cs.	Spreading pressure, (dynes/ cm.)	Mean toxicity (minutes minimum 5 tests).	Comparative ratings. Test number.								Mean rating order.	
				1.	2.	3.	4.	5.	6.	7.	8.		
A. Gas oil	4·0	14·5	14·2	8	9	3	2	8	8	9	4	6·38	8
B. Gas oil and additive A	4·0	19·0	12·4	5	7	8	2	3	4	7	6	5·02	5
C. Gas oil and additive T	4·0	20·0	12·5	7	5	5	9	5	7	8	7	6·65	9
D. Gas oil and additive T	4·0	25·0	13·8	9	3	5	7	6	6	4	8	6·00	7
E. Gas oil, additive T and 0·01 phenols	4·0	25·0	12·5	—	—	—	—	—	—	—	—	—	—
F. Gas oil, additive T and 0·1 phenols	4·0	25·0	10·0	—	—	—	—	—	—	—	—	—	—
G. Gas oil and additive T	4·0	30·0	10·6	2	2	2	8	4	2	2	5	3·38	3
H. Pressure distillate bottoms	3·3	22·0	7·2	—	—	—	—	—	—	—	—	—	—
I. Gas oil, additive T and kerosine extract	3·3	27·0	11·2	2	5	9	2	1	5	5	9	4·75	4
J. Commercial anti-malarial oil	2·5	11·0	11·6	6	8	3	2	9	9	5	3	5·65	6
K. Kerosine extract	1·8	12·0	8·4	2	3	1	2	3	3	3	1	2·25	2
L. Kerosine extract and additive T	1·8	20·0	8·2	1	1	5	1	1	1	1	2	1·63	1

TABLE V.

Toxicity Tests.

Reference No.	Composition of oil.	Properties of oil.						Toxicity results all tests.				Toxicity results selected tests.			
		Spreading pressure, dynes/cm.	Specific gravity at 60/60° F.	Aromatics, % vol.	Viscosity at 77° F., cs.	Distillation A.S.T.M.		No. of tests.	Average No. of larvæ per test.	Mean toxicity, % kill.	Average deviation, %.	No. of tests.	Average No. of larvæ per test.	Mean toxicity, % kill.	Average deviation, %.
						% at 200° C.	50% at ° C.								
1	Gas oil	10·5	0·845	20	4·0	0	251	7	32	71	6·2	6	32	68	3·5
2	Gas oil and additive " T "	15	0·845	20	4·0	0	251	5	31	68	10·6	3	30	69	5·2
3	Gas oil and additive " T "	20	0·845	20	4·0	0	251	5	30	61	14·6	3	30	58	9·0
4	Gas oil and additive " T "	25	0·845	20	4·0	0	251	7	40	57	18·9	4	33	49	3·8
5	Gas oil and additive " T "	30	0·845	20	4·0	0	251	7	32	44	18·2	5	32	31	5·0
6	Gas oil Edeleanu extract	15	0·953	87	3·78	0	251	6	40	93	9·9	5	40	96	5·9
7	Gas oil Edeleanu extract and additive " T "	25	0·953	87	3·78	0	251	9	40	72	12·4	6	40	77	5·1
8	Gas oil Edeleanu raffinate	4·3	0·820	13	3·97	0	251	4	44	66	26·7	3	46	84	10·8
9	Gas oil Edeleanu raffinate and additive " T "	25	0·820	13	3·97	0	251	9	42	34	17·5	5	47	31	7·6
10	Kerosine	11	0·801	17	1·30	82	182	7	35	85	13·2	5	35	94	4·5
11	Kerosine Edeleanu raffinate and additive " T "	25	0·797	12	1·42	82	182	6	42	78	19·0	4	41	93	2·9
12	Kerosine Edeleanu extract and additive " T "	25	0·867	76	1·23	82	182	6	49	84	6·5	5	54	87	4·6
13	Naphthenic gas oil and additive " T "	27	0·889	24	8·08	0	200	5	35	58	7·1	3	41	58	2·2
14	Naphthenic gas oil and additive " T "	25	0·870	25	3·65	0	270	7	41	80	8·7	5	37	80	4·0
								7	36	76	12·6	5	36	80	3·4
15	P.D. bottoms	22	0·900	—	2·89	15	230								
16	Gas oil, kerosine and additive " T "	25	0·840	10	2·89	20	—	6	43	73	10·0	4	39	65	2·7
17	Gas oil, fuel oil and additive " T "	25	0·858	—	9·49	0	—	3	35	44	20·5	2	37	29	8·9

within ½ inch of the rim, distilled water being used to avoid toxic effects due to chlorine in the line supply. Thirty or more *Aedes œgyptii* larvæ (4th stage) were transferred from the culture vessel to a beaker of distilled water, then to each bowl. Sufficient of the oil to be tested to give a film of 10 microns thickness on the water surface was then added, and allowed to remain for ½ hour. At the end of this period the larvæ were again transferred through the bottle neck and placed in a beaker of distilled water. Larvæ sticking in the oil film were first pushed below the surface with a glass rod. After 24 hours the number of larvæ killed was determined, and expressed as a percentage kill.

The London School of Hygiene and Tropical Medicine method of performing toxicity tests offers decided advantages over the previous method used. In Trinidad the larvæ of *Aedes œgyptii* are more resistant to oils than most other larvæ, and kills of less than 100 per cent are obtained with nearly all oils. Thus a direct comparison of toxicity can be made. The technique of introducing and removing the larvæ through the clean aperture eliminates accidental oiling of the larvæ during handling processes.

The results of a number of tests on a series of oils are given in Table V, together with various properties believed to have a bearing on the toxicity of the oils. Occasional results in a series of toxicity tests with *Aedes œgyptii* differ very widely from the mean. It is recommended by some workers in the field that the obvious wide variations should be omitted in arriving at the mean. This procedure was adopted and the results reported in the second part of Table V. This makes the average deviation much smaller, but does not affect significantly the relative ratings of the oils or the conclusions drawn.

EFFECT OF SPREADING PRESSURE ON TOXICITY.

Using the same basic gas-oil, a series of five oils with different spreading pressures was produced by addition of additive " T " and the toxicity showed a gradual decrease as spreading pressure increased.

TABLE VI.

Additive, % vol.	Spreading pressure, dynes/cm.	Toxicity, %.
0	10·5	71
0·2	15	68
0·3	20	61
0·5	25	57
0·8	30	44

In the toxicity test a number of larvæ become entangled in the oil films, and have to be removed by touching with a glass rod, and it was noticed that the lower the spreading pressure of the oil the more pronounced the tendency to stick. Larvæ thus oiled usually die. The results recorded confirm this observation.

EFFECT OF VISCOSITY ON TOXICITY.

From the same crude source kerosine, gas oils, and a gas oil/fuel oil blend were produced to a standard spreading pressure with varying viscosity. A definite increase in toxicity was observed for decrease in viscosity.

TABLE VII.

Components.	Viscosity at 77° F., cs.	Spreading pressure, dynes/cm.	Toxicity, %.
Kerosine	1·39	25	80
Kerosine and gas oil	2·89	25	65
Gas oil	4·00	25	57
Gas oil and fuel oil	9·49	25	44

EFFECT OF CHEMICAL CONSTITUTION OF PETROLEUM FRACTION ON TOXICITY.

Edeleanu raffinates and extracts of kerosine and gas oil were produced in the laboratory; all samples were blended with additive " T " to a standard spreading pressure and toxicities determined. The differences are less marked in kerosine than in gas oil, probably because the viscosity effect is more pronounced, but definitely higher toxicities are obtained with the more aromatic extracts.

TABLE VIII.

	Viscosity at 77° F., cs.	Spreading pressure, dynes/cm.	Aromatics, % vol.	Toxicity, %.
Gas oil	4·00	25	20	57
Gas oil raffinate	3·97	25	13	34
Gas oil extract	3·78	25	87	72
Kerosine	1·39	25	17	80
Kerosine raffinate	1·42	25	12	78
Kerosine extract	1·23	25	76	84

FILM STABILITY OF MINERAL OILS.

Laboratory observations of the behaviour of oil films spreading on water were made by applying the oil to the surface of distilled water in a chemically clean porcelain dish, the quantity added being equivalent to an even film 10 microns thick. The surfaces was protected from draughts, but no precautions were taken to prevent evaporation. Later it was observed that evaporation produced very marked effects, and the work was repeated using dishes of 15 cm diameter enclosed in a glass vessel in which the atmosphere was saturated with water and oil vapours. The technique of sweeping the water surface with glass barriers described by Zisman [6] was not used, and a small contamination was present which in general prevented expansion of the films to the edge. Thus the small residual film, and not the edge of the vessel acted as the confining medium.

TABLE IX.

Film Stability in the Laboratory.

Oil No. (Table V).	Nature of oil.	Spreading pressure, dynes/cm.	Film stability with evaporation.	Film stability without evaporation.
		•	Oil spread on open dish.	Oil spread on covered dish, with vapour of oil saturating the air.
1	Gas oil without additive.	10½	Tendency for lens formation, giving sharply defined lenses in 24 hours, when the oil film shows thin patches and interference colours. As the film ages (1 to 5 days), it becomes thin and uniform.	Lenses developed slowly, but in 3 hours are not sharply defined. In 1 day the film splits up into large, flat lenses.
5	Gas oil with additive "T."	30	Some slight tendency for lens formation, the lenses disappearing after 24 hours to give a thin film showing interference colours.	Lenses develop slowly, but not sharply defined after 4 hours. In 1 day the film splits up into lenses and a thin layer, possibly mono-layer of oil.
6	Gas oil extract without additive.	15	Irregular, patchy film, lenses formed rapidly and gradually decrease in size (1 to 5 days) due to evaporation.	One stable lens, spreading slightly for a few hours, followed by some contraction in 24 hours.
7	Gas oil extract with additive "T."	25	Irregular, patchy film, lenses formed, decreasing in size (1 to 5 days) due to evaporation.	Incomplete spread to a circular patch nearly filling the dish. Small lenses form rapidly round the edge and become sharply defined, then proceed more slowly, to re-combine, giving fewer lenses with a thin layer (possibly mono-layer) of oil between.
8	Gas oil raffinate without additive.	10	Partial spread to give patchy film, which in 24 hours forms lenses and completely covers the vessel. In 2 days the lenses disappear, leaving a slightly patchy film.	Partial cover of the water surface, giving a film which splits into several roughly elliptical areas, not changing quickly into any more stable arrangement.
9	Gas oil raffinate with additive "T."	25	Partial spread to give a patchy film, which forms lenses and more completely covers the vessel in 24 hours. In 2 days the lenses disappear, leaving a slightly patchy film.	Smooth film for several hours. After 1 day the film has formed large, flat, irregular lenses.
—	Kerosine raffinate without additive.	8	Unstable film, partly spread. Mainly evaporated in 2 hours.	No appreciable spread, one stable lens formed.
11	Kerosine raffinate with additive "T."	25	Partial spread to give an unstable film, mainly evaporated in 2 hours.	Initial spread completely over the water surface. The film then splits into sharp lens, which combine more slowly to give a single lens and a very thin film possibly a mono-layer.
—	Kerosine extract without additive.	13	Rapid formation of lenses. Unstable film, mainly evaporating in 2 hours.	Incomplete spread to give a film which forms lenses within 1 hour. In 1 day a compact lens with a thin layer of oil remained.
12	Kerosine extract with additive "T."	25	Rapid formation of lenses. Unstable film, mainly evaporating in 2 hours.	Initial spread over the whole water surface. The film then breaks into lenses, which re-combine slowly to give a single lens and a very thin oil film, possibly a mono-layer.

TABLE IX.—*continued.*

Oil No. (Table V).	Nature of oil.	Spreading pressure, dynes/cm.	Film stability with evaporation.	Film stability without evaporation.
13	Naphthenic gas oil with additive "T."	27	Complete spread to give a slightly uneven film, which becomes even in 2 hours, and remains unchanged for several days.	Complete spread to give an even film which forms lenses in 2–3 hours. The lenses then recombined more slowly, until after 24 hours, two lenses remained, and in 2 days there was a single lens and a thin layer of oil.
14	Naphthenic gas oil with additive "T" and red dye.	25	Complete spread, followed by rapid formation of lenses in 2 hours, stable to 17 hours. Then the oil re-spreads to give a smooth film, mainly lost by evaporation in 3 days.	Complete spread followed by rapid formation of sharp lenses in ½ hour. Then the lenses recombine more slowly, until in 24 hours only one lens remains, surrounded by a thin layer of oil, probably a mono-layer.
15	P.D. bottoms.	22	Spreads to a patchy, uneven film, re-spreading to a smooth film on standing. This is oxidized and poly-merized in 24 hours to a solid skin, readily broken.	Spreads to a smooth film, which remains stable, becoming oxidised and polymerized to a solid skin.

Films of pure polar substances when allowed to spread on water in a confined area tend to form a stable configuration of lenses separated by a monolayer.[8] Oleyl alcohol was placed on water under similar conditions to the oil-film stability test; an immediate spread was observed, and after a few rapid oscillations a stable lens system was formed in less than thirty seconds. When a small quantity of a polar compound is added to a hydrocarbon oil an initial rapid spread of the former is followed by a slower spread of the oil in a thick layer. This edge effect has been fully described by Zisman.[6] The results obtained with the series of oils of Table V are detailed in Table IX.

EFFECT OF EVAPORATION OF THE OIL ON FILM STABILITY.

In order to obtain reasonable toxicity to mosquito larvæ it is necessary to have viscosities lower than 10 centistokes at 77° F, which means that if available refinery fractions are used, it is necessary to use kerosines, gas oils, or blends of kerosine and heavier fractions. All these are subject to relatively rapid evaporation from thin films under tropical conditions of temperature. With the oils examined it was found that if evaporation were prevented the stable configuration of a few relatively large lenses separated by mono-layers was always obtained, although the other properties of the oil, such as viscosity and chemical composition, varied the rate at which equilibrium was obtained. If evaporation was allowed to take place after the stable form had been obtained, an immediate violent agitation was observed at the edges of the lenses which had the appearance of small droplets moving from the edge and then disappearing in the main bulk of the oil. This effect was often followed by respreading of the lenses.

EFFECT OF CHEMICAL COMPOSITION ON FILM STABILITY.

With normal evaporation a marked difference between oils of different composition was observed. Edeleanu extracts in general give the most

sharply defined lenses, the film formed initially being very unstable and breaking into small lenses rapidly.   Raffinate gas oil gave a more stable thick film than the corresponding extract.   The parent materials gave results between these two extremes.

Effect of Additive Film Stability with Normal Evaporation.

The only additive studied in detail has been additive T, which was used with all the oils shown in Table V.   When an oil of low spreading pressure (from 5 to 10 dynes/cm.) is placed on a bowl it usually forms a thick lens, the area of the lens depending on the cleanliness of the distilled water surface to a large degree, as well as on the spreading pressure of the oil.   Addition of polar material increases the rate of spread and the area covered by the oil.   Higher spreading pressures in the case of oils 1–5, Table V, gave more even films with less tendency for lens formation.   It has previously been reported [1] that increase of spreading pressure decreases film stability, but the present work indicates that this is not always true.   It is possible that the type and quantity of additives present as well as the chemical composition of the basic oil, has an important effect in determining the stability of the film.

Field Application.

Malaria control is based on the elimination as far as possible of adult mosquitoes, and any scheme must aim at eliminating the breeding-grounds of the insects.

Excluding the *Anopheles bellator* problem, effective results are obtained in Trinidad, as in other parts of the world, by an efficient drainage system to remove swamp and other surface accumulations of water.   However, complete elimination of surface water is impossible; reservoirs for drinking and industrial supplies must be maintained, drains and streams are necessary for removal of unwanted water, and at periods of heavy rainfall there will be some unavoidable accumulation of small pools.   For these permanent areas of water a larvicide will always be necessary, and in places where a permanent clearance and drainage scheme is not possible because of its high cost, a larvicide is the only solution to the prevention of breeding.   A number of the oils examined in the laboratory have been examined in the field on three main types of surface water.   The work was undertaken primarily to ascertain the effects of spreading pressure under various conditions because little has been reported on this aspect except from the laboratory angle.

Method of Application.

The most usual method of application is by means of the knapsack type sprayer (Figs. 1 and 2), which consists of a tank containing about 2 gallons of oil strapped to the back of the operator.   Built into the tank is a hand-pump so arranged that it can be operated by up-and-down movements of the right hand to force oil through the sprayer jet held at the end of a hose by the left hand.   To spray the surface of the water the operator walks steadily along the edge and pumps continuously.   The rate of

application is variable, and, because numbers of operators are required in a given area, not susceptible to very close control.

For continuous areas of water and flowing streams the drip method is very efficient and needs little control or labour.   For this a container is set up at a convenient location, and arrangements made to allow a small continous addition of the oil to the water.   Many improvised methods have been used, varying from a small hole in the container to elaborate spreading devices.   A simple drip arrangement was made for the present work by welding a short length of $\frac{1}{4}$-inch pipe into a standard drum bung, and inserting a piece of cotton wool.   The rate of addition was readily controlled by manipulating the cotton-wool plug.   The advantage of this device is that it does not involve the transfer of the oil from the shipping container.

APPLICATION TO POOLS IN WATERLOGGED GROUND.

During the rainy season pools form on low-lying ground and provide suitable breeding areas for mosquitoes.   The pools are usually shallow, and vegetation breaks up the water surface.   Oil is usually applied by means of the hand-sprayers at regular intervals.   The series of gas oils of various spreading (Oils 1–5, Table 5) and the commercial oil (Oil J, Table 4) were observed under these conditions.   With spreading pressures below 20 dynes/cm the oil would not spread to a continuous film and clear water spaces were observed, especially around blades of grass.   With spreading pressures of 25 dynes/cm and over the film spread and left no clear areas. It was also observed that the higher-spreading pressure oils were much more effective in killing weeds and grass.   This effect is most probably caused by the greater ability of a high-spreading pressure oil to spread over the moist surfaces of weeds and grass, and also to its ability to cover contaminated surfaces more completely than a low-spreading pressure oil. Evaporation of the gas-oil produced in about 4 days iridescent films with an almost solid appearance, which with spreading pressures over 20 dynes/cm reformed after mechanical agitation.   The total life of the film was 7 to 10 days, after which no residues could be seen.   The commercial oil, which was a blend of kerosine extract and fuel oil, had a good initial spread, but rapid evaporation of the kerosine extract produced viscous non-spreading residues and left clear water after a few hours.

APPLICATION TO A TYPICAL BREEDING AREA.

The camp and refinery area of the United British Oilfields at Point Fortin has been cleared over an approximate radius of $1\frac{1}{2}$ miles facing on the sea.   Swamps have been drained, and the major part of the surface water is removed by concrete-lined drains and culverts.   Favourable breeding areas have been reduced to a minimum, and as a result it was not possible to obtain suitable sites for experimental observation of the effects of oils as larvicides, there being no places in which a regular breeding of *Anopheles aquasalis* could be expected.   On the coastal region south of the cleared area in the direction of Cap-de-Ville, three drains were located in secondary growth bush which appeared to be typical of many areas in Trinidad ; *Anopheles aquasalis* larvæ were found in large numbers, and breeding
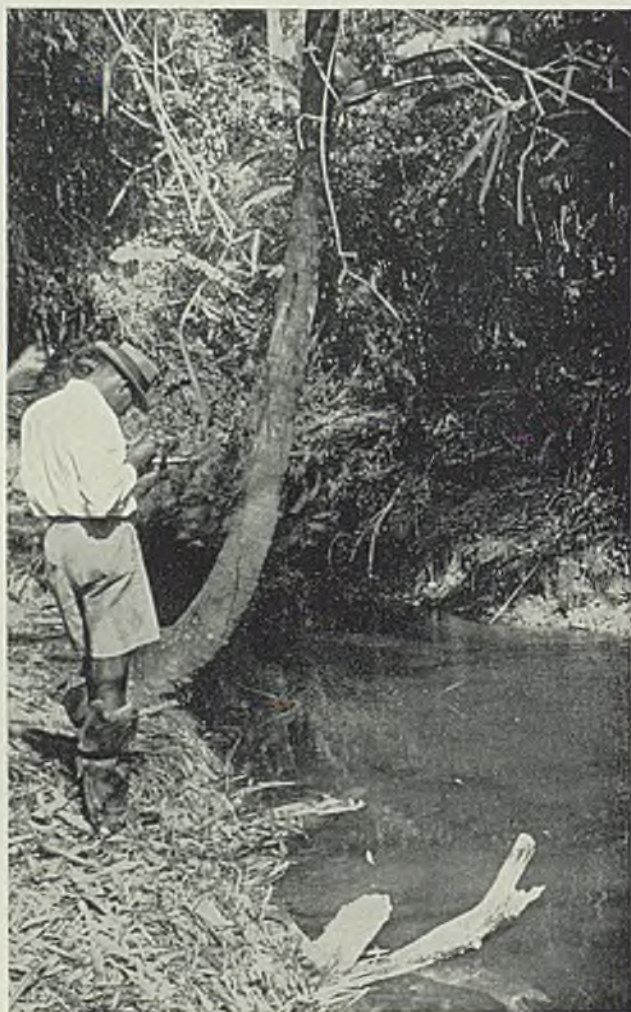
Fig. 1.

Fig. 2.

Fig. 3.

recommenced rapidly after killing all larvæ.   The drains were in the main natural, but an attempt at partial clearance work had apparently been carried out some years ago;   at the upper end they were only 2 to 3 feet wide, and slowly increased in width to 10 to 20 feet at the seaward, and with a length of 300 to 400 yards.   During the dry season in which the work was carried out the flow was sluggish, and the seaward ends were closed with a sand-bar.   Sea-water washed over this bar at high tide and maintained concentrations of sodium chloride between 15,000 and 25,000 mgm/litre. The surface was for the most part shaded by bamboo and palms.   Typical views are shown in Figs. 1, 2, and 3.   Before testing an oil, estimates of the density of *Anopheles aquasalis* larvæ were obtained by taking dip samples of about 300 cc, counting the larvæ, and averaging the results of twenty to thirty dips.   After applying the oil, daily counts were made in the same manner until fresh breeding could be detected. The data obtained at various times during the course of the experiments are recorded in Table X.

TABLE X.

Breeding Conditions of Anopheles aquasalis *on Drains near Point Ligoure.*
Typical dry season breeding conditions in Trinidad.

Drain.	Date. 1945	Area of drain, sq. ft.	Temperature of water, ° C.	Salinity (parts sodium chloride per million).	A. aquasalis larvae counts, average per dip.
No. 1	March 13	5850	28	14,600	26
	March 27	5850	—	14,000	9
	April 10	5850	—	—	5
	April 26	5850	—	14,840	9
No. 2	March 13	2100	30	20,700	4
	March 27	2100	—	23,400	4
	April 10	2100	—	18,500	5
No. 3	March 13	3700	29	21,700	20
	March 27	3700	—	24,000	10
	April 10	3700	—	—	8
	April 26	5000	—	20,910	7

Tests were carried out in these drains using the gas-oils of various spreading pressures (Oils 1–5, Table V) and P.D. bottoms.   The latter was used because favourable results had been reported by Lord [1] and a comparison was desired with the entirely different chemical type.   It should be noted that the oils 1–5 are slightly lower in toxicity by laboratory test than the napthenic type gas oil (Oil 14), probably because the aromatic content is lower.   They were chosen deliberately in an effort to obtain an evaluation of the spreading pressure effect in a range on which measurable laboratory toxicities are obtained.   With a series of oils based on the gas oil of oil 14, laboratory toxicities in the range 80–100 per cent had been obtained, and although this type of oil is obviously better for general work, the fact that 100 per cent kills could be obtained did not allow comparisons to be drawn so readily, because the upper limit of the adopted scale of toxicities was sometimes exceeded.   The laboratory films stabilities of the two gas oil types were not appreciably different.

Each oil was tested once on each drain, three tests being carried out simultaneously; this eliminated possible variations in water and wind conditions. Between each application approximately two weeks were allowed to elapse to enable breeding to recommence. The oil was first applied by means of the hand sprayers at a rate of approximately 3 ml/sq. ft. and with the exception of the wide area at the mouth of one drain the surface could be reached directly with the sprayers. This rate corresponds to a theoretical film thickness approximately three times that employed in the laboratory technique, but was the lowest practical rate at which the oil could be applied with the sprayers used.

All the oils exhibited the edge effect reported by Zisman [6] in advance of the sprayers; small pieces of leaves and other debris travelled along the surface. With no wind blowing an even, continuous film was produced with all the gas oils, even at 11 dynes/cm spreading pressure. As soon as any wind occurred the oil moved with the wind if the width of the drain was more than about 6 ft, leaving clear water. There was some evidence that the higher-spreading pressure oils 20 to 30 dynes/cm resisted this disturbance better than the others, but it could not be described as conclusive.

If the wind dropped, spreading started again and covered the clear spaces. With the P.D. bottoms an initially good spread was obtained, but the film became patchy, and clear areas of water appeared in about 10 minutes. Wind effects were similar to those with gas-oils. In all cases no larvæ could be detected in the drains after an interval of 24 hours, and breeding was first detected after 6 to 8 days. Based on the experience in small pools it was expected that the film would be observable at various stages, but in most cases after 24 hours there was no sign of a continuous oil film. In some instances the oil had blown with the wind to one end of the drain, and in other cases had been flushed away almost completely by the sea breaking over the barrier sandbank. The flow of water with a dropping tide was apparently insufficient to wash out the larvæ.

The rapid complete kills with all the oils tested are in line with the original laboratory toxicity tests (Table IV), which were carried out on similar larvæ removed from local breeding areas. Under the conditions of hand spraying in areas where all the water surface can be reached with the spray, spreading pressure does not appear to be of importance in the control of *A. aquasalis*.

Because breeding recommenced in approximately one week, the interval between spraying should not be more than ten days if complete elimination of breeding is to be obtained. It is therefore an advantage if continuous oiling can be used, and in order to investigate this three drip-cans were set up with Oils 1, 3, and 5. The rate of oil addition in each case was 5 ml/minute. Immediately around the point of addition no perceptible difference in the appearance of the oil films could be detected, they each showed rapid spread with changing interference colours. Wind and current caused the oils to move about as in the spraying experiments with the oil tending to adhere to vegetation at the edges. After 24 hours no mosquito larvæ could be detected, and this condition was maintained over several weeks. The drip-cans required only occasional attention from one man.

After two or three days differences were noted in the main oil films :

the 11 dynes/cm spreading pressure oil gave rather patchy films, but the 20 and 30 dynes/cm oils gave even films with no small clear areas. Where the drains were wider and wind effects occurred the best adherence to vegetation at the edges was obtained with higher-spreading pressures.

On these relatively small areas the oil consumption by the spraying method was 0·4 gal/day, and by the drop method 1·5 gal/day. The latter could probably be reduced by further experiment, because, as discussed in the following paragraph, an area almost ten times as large could be satisfactorily oiled at the same rate of addition by the drip method.

APPLICATION TO LARGER AREAS OF WATER.

It has been stated that a high-spreading pressure would be a disadvantage on large areas of water because in general the edges are the only breeding-places, and the higher-spreading pressure oils would involve the unnecessary oiling of the deep water. In order to obtain information on this subject an experiment was carried out on a water reservoir 450 yards long and 300 yards wide containing forest surface water. The edges were overgrown with grass and for about 20 ft from the edge were reeds and other water-plants. A few *culicine* larvæ but no *anophelines* were observed around the edges; the deeper water was well populated with fish, and presumably no mosquito larvæ were present.

A drip-can was set up with 25 dynes/cm spreading pressure gas oil (Oil 14, Table V) and application made at the rate of 5 cc/minute. The prevailing wind was from the opposite side of the area to the drip location, and with light breezes the oil film spread out to about 25 ft, at right angles to the bank, and then parallel to it. When the wind dropped, which was almost invariably the case at sunset, the oil film then spread over a much larger area, and few clear areas could be observed; reappearance of the wind subsequently compressed it back to the edges. After one week the oil had spread completely between the vegetation at the edges of the area, and evaporation had produced a dark, iridescent film, which could not be permanently broken by agitation. No larvæ were then detectable.

It would therefore appear that a high-spreading pressure is advantageous under these conditions. With spreading pressure up to 30 dynes/cm the oil will not spread against the wind, or remain in place unless anchored by vegetation, but in times of calm spread takes place, and the final effect is to produce a film anchored to the sides where breeding takes place. By use of the drip method rates of application and labour costs are low, and excessive oiling of the deep water does not take place.

DESTRUCTION OF VEGETATION.

Anopheles aquasalis usually breeds in the shade, and therefore, for this and similar shade types, it is an advantage if, in addition to killing the larvæ, the oil will also kill grass and weeds growing in the water and at its edges. Oils 13 and 14 showed excellent properties in this respect, and rapidly killed all vegetation close to the surface in swamps and drains. In addition, they have been used to advantage in preventing the growth of grass and weeds on the sides of drains above the water-line by means of a

light spray at the rate of 8 ounces per 100 square feet.   In earthen drains this reduces the cost of frequent grass clearing, but does not destroy the binding effect of the roots.   The oils were not injurious to large plants.

Conclusions.

The requirements for a mosquito larvicide are, that it should kill all larvæ in the areas treated, and have a residual effect preventing further breeding for as long as possible.   In addition, it should not be toxic to man or animals.   In certain cases it is desirable for the larvicide to kill weeds and grass providing shade for larvæ, but in other cases, such as rice-fields, vegetation should not be harmed.

The factors involved in the manufacture of a petroleum oil meeting these requirements require a compromise :—

(1) An oil with a low viscosity is desirable for rapid penetration of tracheæ of larvæ.   However, the lower the viscosity the more volatile the oil, and thus the less the film stability and durability ;

(2) The spreading pressure should be high in order to produce more complete spread over contaminated surfaces and films more stable to wind and mechanical displacement under field conditions.   In contrast, an increase of spreading pressure gives a decrease in toxicity under laboratory conditions.

(3) Use of a highly aromatic oil or a cracked material such as P.D. bottoms, gives a highly toxic oil.   However, film stability is poor with aromatic fractions, and with P.D. bottoms rapid oxidation and polymerization may occur in the field to give incomplete films.

In general, no field experiments have indicated a correlation between the laboratory film stability test and field conditions.   Because the effect of evaporation is so pronounced any conclusions from laboratory observations should be treated with caution.

Where mechanical removal of the films by flowing water or wind occurs hand-spraying is effective only if carried out at intervals of one week, but excellent results can be obtained by a continuous drip application.   For this latter method spreading pressure of order of 25 dynes/cm are very effective.

Satisfactory results over a period of 2 years have been obtained in South Trinidad by a Malaria Control Unit operating under normal conditions which could be expected to apply to an estate or Government unit using an oil for which the specification limits are represented by oils 13 and 14 (Table V).   These oils were manufactured from typical Trinidad naphthenic crudes by adding a petroleum derived additive to gas oils.

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DISCUSSION.

DR. A. R. RICHARDS : I notice in all the tables that the laboratory tests were all carried out with a film thickness of 10 microns, whereas the field tests were estimated to have thicknesses of 30 microns.   I am wondering whether the oil thickness has any effect on toxicity ; if it is just a blanket effect of removing oxygen then a thinner film would be just as effective. It occurs to me that the differences in film thickness may account for differences between field and laboratory results.

MR. HAZZARD : In some cases the thickness of the film will have a pronounced effect.   All larvæ have to come to the surface to breathe, and obviously if the film thickness is so great that they cannot penetrate it with their breathing tubes toxicity will be increased.   The aim of every worker in the field is to produce as great a thickness of oil film as is possible, and to keep it permanently on the water surface.   The reason we used 10 microns in the laboratory was that this had been used by other workers, and was specified by the Medical Research Council's specification for anti-malarial oils for the Armed Forces.   Our results should therefore be comparable with those of other workers.   We also endeavoured to obtain the same film thickness in the field, but with the sprayers used, even though the men were made to walk as fast as possible and to pump slowly, we could not get below an average of 30 microns.   The figure is, of course, an average ; the pronounced effect of wind has been shown, and in practice in the field all thicknesses down to a monolayer are seen at different times.   The important thing is to have a sufficient supply of oil of suitable spreading characteristics so that when the wind drops the area of water is covered again.

MR. L. T. WINKLER : I understand that one of the objects of this work was to correlate spreading pressure and the usefulness of the oil as a mosquito controlling agent in the field.   In the laboratory, distilled water was used for all the spreading experiments, whereas in the field the water would be entirely different, and different behaviour of the oil might be obtained on different water surfaces.

MR. CROSSFIELD : If dirty field water were used in the laboratory comparative results could not be obtained because the surface tension would be variable and not susceptible to control.   Distilled water was therefore used, and it is also of importance to avoid the toxic effects of chlorine from line supplies in the toxicity tests.

DR. PIERRE : In continuation of the last speaker, I am wondering whether field water could be used if it were filtered. Also I notice that most of the field experiments have been carried out in the dry season, when the amount of mosquito breeding is limited and can be more easily kept under control, whereas in the wet season, particularly towards its end, we get an accumulation of larvæ in swampy pools. Under these conditions water surfaces may be entirely different, and I should like to know how the oils behave under these conditions.

MR. CROSSFIELD : If a spreading oil is placed on a contaminated water surface, the contaminating film is compressed until a balanced state is obtained.

MR. HAZZARD : The higher the spreading pressure of the oil, the more the oil will spread. In the laboratory, where you have a rigid confining medium in the edge of the bowl, the effect is readily observed, in the field we more often obtained complete spreads, and I think this is most probably caused by the spreading oil pushing the contamination on the water surface into the soil on the banks of the stream or pool. Rainy season experiments were the first of the three field trials reported in the paper.

DR. WARDELL : Can you tell me if the addition of an oil-soluble poison would increase the toxicity or would impair the spreading quality of the oil.

MR. HAZZARD : If the compound added were polar it would tend to increase the spreading pressure. As regards toxicity, we did add phenols to a 25 dynes/cm oil (Table IV, Oils E and F). There was a slight improvement in toxicity, but with the larvæ available locally killing times with oil are so short that the addition of other toxic material did not seem justified.

DR. RICHARDS : Is it correct that the mosquito has to lay its eggs from solid ground ?

MR. HAZZARD : It has to be anchored while laying its eggs.

DR. RICHARDS : That is the reason why you want the oil to cling around the edges of your water surfaces. Now is the main idea to repel the laying mosquito or to kill off the larvæ.

MR. HAZZARD : Anything which interrupts the life cycle of the mosquito is of use in the control of malaria. We believe that if the oil is produced so that it will close up on vegetation and not leave clear spaces then the adult will have difficulty in finding a place to deposit her eggs in the particular body of water, and also that any larvæ will also have difficulty in finding a place to come to the surface for breathing.

THE DETERMINATION OF ORGANIC PEROXIDES IN HYDROCARBONS.

By E. M. Tanner and T. F. Brown.

Summary.

In an attempt to find a method suitable for the estimation of organic peroxides of the type R–O–O–R′ in hydrocarbon oils, several methods of peroxide determination published in the literature were tested. The results obtained were very low, and a method specially suitable for hydrocarbon oils was developed, based on the reduction of the peroxide by ferrous ammonium sulphate in an inert atmosphere and subsequent titration of the excess ferrous salt with standard potassium dichromate solution. The method has also been extended to the determination of peroxides formed in cracked gasolines.

Introduction.

For a programme of research on organic peroxides in hydrocarbon oils it became desirable to have available a reliable method for the estimation of the amounts present. Three methods of determination of organic peroxides reported in the literature [1,2,3] were therefore tested using blends containing known amounts (up to 3 per cent) of various peroxides in straight-run gas oils. Details of these tests are given in Section I. The results were consistently low, and it became apparent that either existing methods would have to be modified or that a new method would have to be developed.

Since cracked oils contain a considerable quantity, and straight-run gas oils frequently contain traces, of unsaturated hydrocarbons, and, moreover, as the peroxide might, conceivably, be of an unsaturated nature, methods which would involve the liberation of iodine from potassium iodide were not further developed owing to the absorption of iodine which would occur under these conditions. The method described in Section II, like several methods reported in the literature, is based on the oxidation of ferrous salts, and has been found convenient in that, while having an accuracy of about ± 4 per cent, it avoids the tedium of titanous chloride titrations employed in some methods,[2,3] but at the same time requires no special apparatus in the form of a filter photometer or spectrophotometer which is necessary for the various colorimetric methods now in use.[3,4,5]

It was also found that a modified form of the method was useful for the determination of hydrocarbon peroxides in " aged " gasolines, especially where the peroxide content was fairly high, and this extension of the method is described in Section III.

I.—Estimation of Organic Peroxides in Hydrocarbons by Various Methods.

Three methods were tested in order to establish whether any one could be used, without further modification, for the estimation of from 1 to 3 per cent of organic peroxides in distillate oils. The methods selected were those

of : (a) the Institute of Petroleum,[1] (b) Yule and Wilson,[2] (c) Lea.[3] The
results were disappointingly low, and are shown in Table I. Consequently

TABLE I.

Determination of Organic Peroxides in Gas Oils by Various Methods.

Method.	Peroxide.	Percentage (wt/wt) of individual peroxide in straight-run gas oil.		Peroxide number, mgm equivalents of active oxygen per kgm.	
		(a) Added.	(b) Found.	(a) Added.	(b) Found.
I.P.[1]	Acetyl peroxide	0·95 *	0·20	161	34
,,	*tert*-Butyl hydroperoxide	2·52	1·31	560	292
,,	Lauroyl peroxide	1·66	0·05	79	2
,,	Benzoyl peroxide	1·04	0·45	86	37
Yule and Wilson [2]	Acetyl peroxide	0·95 *	0·62	161	105
,, ,,	*tert*-Butyl hydroperoxide	2·52	1·43	560	318
,, ,,	Lauroyl peroxide	1·66	0·04	79	2
Lea [3]	Acetyl peroxide	0·95 *	0·35	161	59
,, ,,	*tert*-Butyl hydroperoxide	2·66	1·76	591	392
,, ,,	Lauroyl peroxide	1·66	0·13	79	6

* For comparison purposes only ; acetyl peroxide was not isolated but was pre-
pared in the gas oil, its peroxide content being determined by the dichromate method.

it was decided to test whether accurate results could be attained by sub-
stituting cracked gasoline for gas oil, employing a method which was
designed specifically for cracked gasolines.

Table II gives the results obtained by Yule and Wilson's method when

TABLE II.

*Determination of Organic Peroxides in Cracked Gasoline by Yule and
Wilson's Method.*[2]

Peroxide.	Percentage (wt/wt) of individual peroxide in cracked gasoline.		Peroxide number, mgm equivalents of active oxygen per kgm.	
	(a) Added.	(b) Found.	(a) Added.	(b) Found.
tert-Butyl hydroperoxide .	0·90	0·74	200	164
Lauroyl peroxide .	1·52	0·15	72	7
Benzoyl peroxide .	1·72	0·24	142	20

applied to solutions of non-hydrocarbon peroxides in a cracked gasoline
fraction, b.pt. 120° C, Bromine No. 41 ; here again the values found were
much lower than the amounts of peroxide added.

In carrying out experimental work on methods (a), (b), and (c), the
following conditions were observed :—

(a) *The I.P. Method.*[1] This method was designed for ethers, and not
for hydrocarbons, but the technique described for ethers was followed

closely, using straight-run gas oils, except that the titration of 20 ml recommended was never attained, owing to the 10-gm limit on the weight of sample taken.   This method was not attempted with cracked gasoline samples, since some absorption of the liberated iodine by the unsaturated hydrocarbons would have occurred.

(b)   *Method of Yule and Wilson.*[2]   The method described was followed using gas oil and cracked gasoline blends, except that the hydrocarbon samples were weighed and 2 ml were employed instead of 10 ml.

(c)   *Method of Lea.*[3]   The volumetric procedure was carried out, with the exception that the inert atmosphere consisted of nitrogen, and not carbon dioxide.   Tests were confined to gas oil blends only.

Effect of Reaction Conditions on Methods (a), (b) and (c).
Homogeneity of Solution.

The difficulty of obtaining correct values for peroxide content of fats was attributed in part by Lea [3] to the two-phase reaction mixture normally obtained with fats and solutions of inorganic salts.   The same difficulty applies to determinations of the peroxide content of hydrocarbon mixtures. Probably the principal cause of the failure of the Institute of Petroleum iodine method for ethers [1] when applied to solutions of non-hydrocarbon peroxides in hydrocarbon oils and of the Yule and Wilson method [2] when applied to similar blends in gas oils or cracked gasoline lies in the fact that inadequate contact is obtained between the reactants.   This fact was illustrated in the case of the I.P. method.   A blend containing 1·29 per cent (wt/wt) benzoyl peroxide in di*iso*propyl ether was submitted to a peroxide determination by the exact I.P. method.[1]   The reaction mixture was homogeneous, and the value obtained was 1·28 per cent.

Thus the heterogeneous nature of the reaction mixture appears to be the chief reason for the failure of the I.P. method when applied to solutions of non-hydrocarbon peroxides in gas oils.   It is probably also the reason for the failure of the Yule and Wilson method with similar blends.   However, this latter procedure was developed for very small concentrations of peroxides formed by autoxidation in cracked gasoline, and such peroxides are more readily decomposed by ferrous salts than the non-hydrocarbon peroxides employed in the determinations.   The combined effects, therefore, of higher peroxide concentration and of different peroxide type employed in the present work would be expected to act adversely on the accuracy of the method.

Reaction Time.

A test by the I.P. method on a solution containing 2·18 per cent *tert*-butyl hydroperoxide in di*iso*propyl ether gave results varying from 1·14 to 1·32 per cent, according to the speed of the titration.   In each case severe " after-blueing " occurred, which suggested that the reaction time of 10 minutes was insufficient for this particular peroxide.   This point was confirmed by allowing the homogeneous reaction solution (both " test " and " blank ") to stand overnight, in place of the 10 minutes' shaking employed in the I.P. method.   The result obtained was 2·24 per cent of *tert*-butyl hydroperoxide, and no " after-blueing " occurred.   The slow reaction

O O

of this peroxide with potassium iodide has been noted by other workers,[6] and should not be considered as casting any reflection on the reaction time of the I.P. method, as the peroxides formed in the autoxidation of ethers are much more readily decomposed.

Oxygen Concentration.

The most probable explanation of the low results given by Lea's method with gas oils is the possibility, not overlooked by Lea himself [3] in his work on the peroxide contents of edible fats and oils, that the presence of free oxygen is necessary for the completion of the reaction between peroxides and ferrous salts. In his procedure a rigorous de-aeration of the reaction mixture is carried out, and in view of the authors' experience in developing the present method (see Section IVa), this would appear to be liable to produce low results.

II.—ESTIMATION OF ORGANIC PEROXIDES IN GAS OILS BY DICHROMATE METHOD.

Scope of Method.

The method is applicable to the determination of 0 to 3 per cent of organic peroxides of the type R–O–O–R' in gas oils, where R represents hydrogen, an alkyl or an aryl radical, and R' is either an alkyl or an aryl group.

Reagents.

   (a)   Glacial acetic acid as solvent.
   (b)   N/10 Ferrous ammonium sulphate solution.
   (c)   N/50 Potassium dichromate solution.
   (d)   Solution consisting of 30 ml phosphoric acid (sp. gr. 1·7)
                              30 ml sulphuric acid (98 per cent)
                              Water added to 200 ml.
   (e)   Diphenylamine indicator—0·5 gm diphenylamine in 50 ml sulphuric acid (98 per cent).

Procedure.

0·5 ml of the gas oil to be tested is weighed into a 100-ml conical flask, the air of which has previously been displaced by nitrogen. 65 ml of glacial acetic acid, which has been de-aerated by passage of a stream of nitrogen from a cylinder for 5 to 10 minutes, are added, and to the homogeneous mixture so obtained 5 ml of N/10 ferrous ammonium sulphate solution (de-aerated with nitrogen) are run in from a small burette. The air in the headspace above the liquid is displaced by a brisk stream of nitrogen from a cylinder for 1 to 2 minutes, the nitrogen supply is considerably diminished, and the reaction mixture is heated in a water bath at 60° to 70° C for 15 minutes. At the end of this time the mixture is cooled, transferred to a 250-ml conical flask, and diluted with approximately 60 ml distilled water. 10 ml of solution (d) are then added followed by 4 or 5 drops of indicator (e). The mixture is titrated with N/50 potassium dichromate solution, the colour change being through various shades of green to an intense violet-blue. A blank test is made with each batch of reagents.

The percentage of the peroxide present is then readily calculated from the formula :—

$$x = \frac{0 \cdot 05(a - b)fNM}{w}$$

and the peroxide number by :—

$$y = \frac{1000(a - b)fN}{w}$$

where

x = Percentage of peroxide present (wt/wt).
y = Peroxide number in mgm equivalents of active oxygen per kgm.
a = ml of standard potassium dichromate solution in blank.
b = ml of standard potassium dichromate solution in test.
N = Normality of potassium dichromate solution.
f = Normality factor of potassium dichromate solution.
w = Weight of sample used (gm).
M = Molecular weight of peroxide.

Results with Gas Oils.

The results of determinations, by the dichromate method, made on solutions of various peroxides in straight-run gas oils in concentrations up to 3 per cent are presented in Table III.

TABLE III.

Determination of Organic Peroxides in Gas Oils by the Dichromate Method.

Peroxide.	Percentage (wt/wt) of individual peroxide in straight-run gas oil		Peroxide number, mgm equivalents of active oxygen per kgm.	
	(a) Added.	(b) Found.	(a) Added.	(b) Found.
tert-Butyl hydroperoxide . .	1·90	1·93	422	429
,, ,, . .	2·66	2·67	591	593
Lauroyl peroxide . . .	1·83	1·79	87	85
,, ,, . . .	2·42	2·48	115	118
Benzoyl peroxide . . .	1·17	1·16	97	96
,, ,, . . .	1·52	1·54	126	127

Benzoyl peroxide was the only pure peroxide available. The *tert*-butyl hydroperoxide and the lauroyl peroxide were both commercial samples, their purity being 58·0 and 32·2 per cent (wt/wt) respectively, as estimated by the method of Marks and Morrell,[7] which is specific for high concentrations of peroxides of this type, and depends on the liberation of iodine from potassium iodide.

Two methods of expressing the results of the peroxide estimations have been employed in each of the tables throughout this work—namely, the percentage by weight of the individual peroxide, and the peroxide number. The latter has obvious advantages in mixtures of peroxides or where the peroxide structure is of an unknown nature, as in autoxidized cracked fuels.

Some confusion exists in the literature over the term " peroxide number," each author using his own particular definition of this quantity. For

example, the Institute of Petroleum define their peroxide value of ethers [1] as the number of milligram equivalents of oxygen per gram of sample, Lea [3] as milligram equivalents per kilogram, while Yule and Wilson [2] adopt the entirely different procedure of measuring the number of gram equivalents of active oxygen per 1000 litres of gasoline.   Alternative methods of recording quantities of peroxides in solution are milligrams of peroxidic oxygen per ml of solution (Bolland *et al.*[4]) and parts per million of active oxygen as employed by Robey and Wiese.[8]

Throughout the present work, however, the peroxide number is always expressed as the number of milligram equivalents of active oxygen per kilogram of sample, and these values have been calculated to the nearest whole number; in this way all the peroxide values appear as integers, and no decimalization is necessary in the concentration range adopted.

The accuracy that can be expected with the dichromate method is of the order ± 4 per cent.

III.—Extension of the Dichromate Method to the Estimation of Peroxides in Cracked Gasoline.

Scope of Method.

The method is applicable to the determination of peroxides that have been formed by autoxidation in cracked gasoline, and is especially suitable where the peroxide content is fairly high.   It is also applicable to the estimation of non-hydrocarbon peroxides of the type R–O–O–R' in synthetic mixtures in hydrocarbons boiling in the gasoline range.

Procedure.

The method is similar to that described for gas oils, except that the volume of acetic acid is reduced from 65 ml to 40 ml, and the reagents are not de-aerated, provided that the ferrous ammonium sulphate solution is a freshly prepared sample.

In the determination of the peroxide content of " aged " gasolines the reaction mixture may be allowed to stand 15 minutes at room temperature in place of heating at 60—70° C for 15 minutes.

Results with Gasoline.

Estimations were carried out on a cracked gasoline fraction, boiling range 120—126° C, which had become autoxidized by standing in a pyrex flask in sunlight for several months, and on blends of this material with a straight-run gasoline fraction boiling in the neighbourhood of 98° C.   Fig. 1 shows the linear variation of peroxide numbers found with weight percentage of cracked gasoline.   This was the first indication that consistent results were given by the dichromate method for cracked gasolines.   A similar relationship was also found by Lea [3] for edible fats and oils.   But a linear relationship is not sufficient evidence that the results obtained are the absolute values.   This is demonstrated by Fig. 1, in which two lines are shown which were obtained experimentally for the same series of blends, depending on whether the estimations were carried out in air or in nitrogen. Further reference will be made to this later.   Evidence that the line for nitrogen gave the correct results was acquired as follows.

Blends of *tert*-butyl and lauroyl peroxides were prepared in a cracked gasoline fraction, b.pt. 120° C, bromine number 41. Benzoyl peroxide, however, being very sparingly soluble in gasoline, was blended in a mixture of 50 per cent (vol.) benzene and 50 per cent (vol.) of the cracked gasoline.
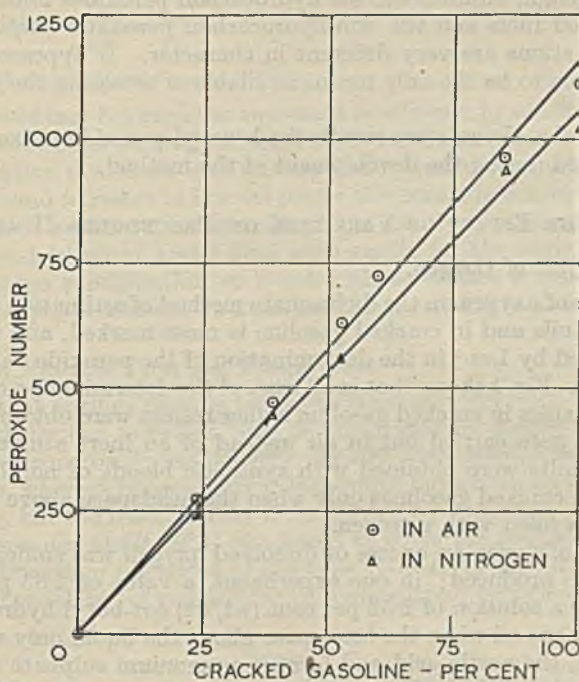

Fig. 1.

DETERMINATION OF PEROXIDE NUMBERS OF CRACKED GASOLINE.

TABLE IV.

Determination of Organic Peroxides in Hydrocarbons Boiling in the Gasoline Range by the Dichromate Method.

Peroxide.	Hydrocarbon.	Percentage (wt/wt) of individual peroxide.		Peroxide number, mgm equivalents of active oxygen per kgm.	
		(a) Added.	(b) Found.	(a) Added.	(b) Found.
tert-Butyl hydroperoxide .	Cracked gasoline	1·59	1·56	354	346
Lauroyl peroxide . .	,, ,,	2·52	2·53	119	125
Benzoyl peroxide . .	,, ,,	4·14	4·20 *	342	347
,, ,, . .	Benzene	9·44	9·62	780	795
,, ,, . .	,,	4·43	4·43	366	366

* Obtained by allowing the reaction mixture to stand 4 hours at room temperature.

Experimental determination of the peroxide contents of these blends by the method described above, gave reasonable agreement with the amounts added, as can be observed from Table IV. Hence it would appear that the peroxide numbers obtained for the nitrogen line in Fig. 1 are the correct values, although, admittedly, the hydrocarbon peroxides found in autoxidized cracked fuels and the non-hydrocarbon peroxides employed in the above estimations are very different in character. It appeared, however, to the authors to be the only means available of assessing the value of the method.

Table IV also shows some results for benzoyl peroxide in benzene which were obtained during the development of the method.

IV.—THE EFFECT OF VARIABLES ON PROCEDURES II AND III.

(a) The Effect of Oxygen.

The effect of oxygen on the dichromate method of estimation of peroxides both in gas oils and in cracked gasoline is most marked, and is similar to that observed by Lea [3] in the determination of the peroxide value of edible fats and oils. Fig. 1 shows that in all cases of the determination of the hydrocarbon peroxides in cracked gasoline higher results were obtained when the estimations were carried out in air instead of an inert atmosphere; and accurate results were obtained with synthetic blends of non-hydrocarbon peroxides in cracked gasolines only when the headspace above the reaction mixture was filled with nitrogen.

With gas oils even an excess of dissolved oxygen was sufficient for high results to be produced; in one experiment, a value of 2·83 per cent was obtained for a solution of 2·52 per cent (wt/wt) tert-butyl hydroperoxide in straight-run gas oil when the headspace above the liquid only was replaced by nitrogen, the acetic acid and ferrous ammonium sulphate solution not having been de-aerated. Using a similar technique, a value of 2·21 per cent was obtained for a solution containing 1·66 per cent lauroyl peroxide; it is assumed that this effect is due to the autoxidation of small quantities of olefines present in the gas oil and of readily autoxidizable hydrocarbons of the tetralin type.

This autoxidation effect is induced by the peroxides, as no autoxidation was obtained with gas oils or with cracked gasoline under the same conditions, in absence of peroxides; but the relative ease of autoxidation of the hydrocarbons present also contributes to the effect, as this was not observed in estimations of non-hydrocarbon peroxides in solvents such as benzene.

On the other hand, when experiments were carried out with care being taken to exclude all traces of oxygen during the whole estimation, low results were obtained. This effect was very pronounced with tert-butyl hydroperoxide; a result of 1·78 per cent being obtained in one instance when the actual concentration was 2·66 per cent of the peroxide in gas oil. Low results were obtained also with cracked gasoline blends under the same conditions. Reference has been made, in Section I, to Lea's suggestion [3] that the presence of free oxygen may be necessary for the reaction between ferrous salts and organic peroxides to proceed to completion; and this appears to be the most probable explanation of the low results obtained

with the dichromate method under thorough de-aeration of the reaction system.

Therefore, in developing the dichromate method, a compromise had to be made between excluding all, or retaining too much, oxygen. The experimental conditions described above for de-aeration were those which gave results that approximated most closely to the theoretical.

(b) *Effect of Acetic Acid Concentration.*

Adequate contact between the reactants is attained by ensuring that the acetic acid solution is perfectly homogeneous before the ferrous ammonium sulphate solution is added; any undissolved hydrocarbon particles at this stage were found to result in low values for the peroxide content, but 65 ml of glacial acetic acid were found sufficient to dissolve 0·5 ml of all the gas oils tested, and 40 ml of acetic acid were ample for the same quantity of gasoline. Some precipitation of a solid phase occurs when the ferrous ammonium sulphate solution is added, but this was found to be unimportant.

(c) *Effect of Reaction Time and Temperature.*

The fact that various organic peroxides react at widely different rates in solution with ferrous salts has been demonstrated by Robey and Wiese.[8] *tert*-Butyl hydroperoxide reacts very rapidly with ferrous salts at room temperature, whereas benzoyl peroxide requires more than an hour at room temperature, but the reaction may be expedited by warming. The reaction time of 15 minutes at 60–70° C was found to cover the requirements of all the non-hydrocarbon peroxides of the type R–O–O–R' tested.

Table V gives data for estimations of hydrocarbon peroxides carried out

TABLE V.

Effect of Reaction Time and Temperature on Determination of Hydrocarbon Peroxides in Cracked Gasoline.

Sample No.	Percentage $-O_2-$ group (wt/wt). Found.	Peroxide number, mgm equivalents of active oxygen per kgm. Found.	Reaction conditions.
3	0·87	544	$\frac{1}{4}$ hr. at 20° C.
3	0·88	550	$1\frac{1}{2}$ hr. at 20° C.
3	0·87	544	$\frac{1}{2}$ hr. at 50° C.

on one sample of cracked gasoline, and shows that a reaction time of 15 minutes at room temperature is sufficient for this type of peroxide, any increase of temperature or of reaction time not affecting the results provided that an atmosphere of nitrogen is maintained throughout the reaction period. The comparative ease with which these autoxidized peroxides in cracked gasoline react with ferrous salts is due to the fact that cyclic olefines form peroxides of hydroperoxide structure,[9, 10] possessing the highly oxidative hydroperoxidic ·OOH groups and this constitution is probably typical also of the peroxides formed by other olefines.[11] In contrast, peroxides containing the non-hydroxylic ·O·O· groups are much less

reactive.[9]   The method described is applicable to both these groups of peroxides.

Trimeric acetone peroxide $(C_3H_6O_2)_3$, however, scarcely reacts at all with ferrous ammonium sulphate under the conditions described in Section II, and according to other workers [12, 13] the cyclic structure of this peroxide is the cause of its low reactivity.

ACKNOWLEDGMENT.

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OBITUARY.

WILLIAM SUTTON.

WILLIAM SUTTON, who died suddenly on March 29, 1946, in his seventy-second year, was one of the pioneers of the petroleum industry, and had a wide knowledge of the technology of the industry, particularly from the engineering angle. In 1897–98 he was commissioned by the late Sir Boverton Redwood to design and superintend the erection of a petroleum refinery for the Elsass Petroleum Gesellschaft. In 1901–2 he was engineer in charge of the oil properties of the Texas Oil Fields, Ltd., at Beaumont, Texas. In 1905 he was appointed resident manager of the Californian Oil Syndicate Ltd., at Lompoc, where he remained until 1908, when he became manager of the producing properties at Coalinga of the British Consolidated Oil Corporation, Ltd.

During the intervening periods from 1898 until 1915 he was engaged by Sir Boverton Redwood to examine and report on plant on oil- and gas-fields and on oil-storage installations and pipelines. In this connexion he visited the United States, Mexico, Canada, Egypt, Galicia, Roumanid, Russia, Italy and Germany. He also acted as adviser on the design of plants for the production, refining, storage and transport of petroleum.

During the First World War he acted in an honorary capacity for the Scientific Advisory Committee of the Ministry of Munitions and did valuable work in relation to the extraction of oil from shale and cannel coal.

In 1919 he became a partner with Mr. Arthur W. Eastlake as consulting petroleum engineers and, until his retirement in 1930, again visited petroleum properties and refineries in various parts of the world, including India and the United States.

He became a Member of the Institute on its foundation in 1913 and served on its Council from 1924 to 1932.

A kindly personality, ever ready to help or advise, he made many friends both within and without the industry.   G. S.

EDWARD HUBERT CUNNINGHAM CRAIG.

E. H. CUNNINGHAM CRAIG, the well-known consulting petroleum geologist, passed away on the 24th of April, 1946.

Cunningham Craig was born in Edinburgh in 1874, and was the younger son of Edwin Cunningham Craig. He was educated at Trinity College, Glenalmond, and at Clare College, Cambridge. In 1896 he joined the staff of H.M. Geological Survey, and was elected a Fellow of the Geological Society. His survey experience resulted in joint authorship of two Memoirs, and the publication of papers on Cairngorms, Igneous Breccia of the Lui near Braemar, Metamorphism in Loch Lomond District, and the Squir of Eigg. In 1903 his services were transferred to the Colony of Trinidad and Tobago, as Government Geologist. In this post his experience with the Survey stood him in good stead, and during the next few years he carried

out a large amount of detailed geological mapping, and presented to the Government a series of reports on the oil prospects of the country. In this way his main interest in life was forever fixed on the subject of petroleum geology, and in 1907 he resigned from Government Service, and in August of that year joined the Geological Staff of the Burmah Oil Company. Later in the same year he arrived in Persia and, after examining several areas, wrote a report on " The Oil-fields of Luristan." Early in 1908 he arrived in Burma, and for several years devoted himself with great energy and enthusiasm to the general and detailed examination of the geology of the Tertiary oil-belt of that country. In respect of geological knowledge and experience, mental and physical energy, and independence of judgment, he was outstanding among his colleagues, whom he helped in various ways, notably by instruction in the then up-to-date methods of large-scale geological mapping. It would, however, require more space than is available here to record the work carried out by him in Burma, and to assess its value.

During the hot season in Burma in the year 1910 Cunningham Craig paid a brief visit to Trinidad, as the great interest that was then being taken in the oil prospects of that country had created a demand for his advice and assistance in connection with many concessions for petroleum.

In January 1912 Cunningham Craig returned from Burma to set up as a consulting petroleum geologist in London, and was appointed Geological Adviser to the Burmah Oil Company and the Anglo-Persian Oil Company. He held the latter appointment until 1926, and the former appointment until his death. His well-known book, " Oil Finding," first published in 1912 and revised and enlarged in 1920, contained much information, particularly in regard to large-scale geological mapping, that was of interest and value to the many young academic geologists who in those days were taking up the study of petroleum geology. During the years 1912–14 inclusive he visited South Africa on behalf of the Union Government, and he also carried out investigations in Alberta, Manitoba, and New Brunswick. Early in 1916 he was elected a Fellow of the Royal Society of Edinburgh, and read a paper on " The Origin of Oil Shale " to the Society.

Cunningham Craig was very active during the 1914–18 world war. In 1916 he was representative of the Director, Trench Warfare Supply Department, at three chemical factories; in 1917 he was Senior Geologist, Petroleum Research Department, under the Ministry of Munitions and the Admiralty; in 1917–18 he was Geological Adviser and Chief Officer for the co-ordination of Research and Production, Petroleum Executive; and in 1918 Technical Adviser to the Committee on the production of oil from Cannel Coal, etc. His resignation from the last-mentioned post may have been due to failure on his part to appreciate fully the great practical difficulties of a non-geological nature that would have to be overcome if oil in sufficient quantities was to be obtained from cannel coal and cognate raw materials before hostilities ceased, and might perhaps account for the absence of any official recognition of his considerable war-time services.

In the years succeeding the first world war Cunningham Craig conducted geological investigations in Egypt, Ecuador, and East Indies (including Java), Roumania, Jugo-Slavia, and the United States. During the great financial and industrial depression of the early thirties he was

relatively inactive, but subsequently he resumed his activities, his out-standing investigations being carried out in Turkey on behalf of the Turkish Government.

Cunningham Craig was for many years closely associated with the Insti-tute of Petroleum. He was one of the Founder Members of the Institute, and at the Inaugural Meeting held on March 3rd, 1914, he gave an address on "The Educational Aims of the Institute." He was a member of the Council from 1915 to 1930, and when the Fellowship was instituted he became a Fellow of the Institute. In view of his long and close association with the Institute, Members of the Council at their meeting, held on the 8th of May, expressed deep regret at his passing, and agreed that on their behalf a message of condolence, signed by the President, be sent to Mrs. Cunningham Craig.

Although Cunningham Craig read papers to the Geological Society of London and the Royal Society of Edinburgh, and contributed articles to the *Geological Magazine* and other periodicals, most of the papers by him were read at Meetings of the Institute of Petroleum and published in the *Journal* of the Institute. The first sixteen volumes of the *Journal* contain fourteen papers by him on a variety of subjects, notably on "The Oilfields of Alberta," "The Prospective Oilfields of Barbados," "The Riddle of the Carpathians," "Geophysical Surveys as Aids to the Geologist," "Recent Researches Bearing upon the Origin of Petroleum," "Jet and Jetonized Material," Kerogen, Kukkersite and other oil shales, and various retortable oil-yielding materials of many countries. He also took a prominent part in the discussions of the early geological papers read at the meetings of the Insti-tute. When it is considered that most of the results of his investigations are buried in the files of Government Departments and of oil companies, and have not been published, it will be appreciated that his total output of work was enormous.

It is important to bear in mind that most of Cunningham Craig's pub-lished work was written many years ago during the early days of geological exploration for oil, and dealt with a variety of subjects and with the geology and oil prospects of large and widely separated regions. Great and rapid advances have subsequently been made in our knowledge of these subjects, and an enormous amount of detailed geological mapping and geophysical prospecting has been carried out in areas described by him. His published work should therefore be appraised in the light of the know-ledge existing at the time of publication, and not in the more brilliant and searching light of the knowledge of to-day. It is unfortunate that "Oil Finding" was written at the outset of his career as a Consultant, and was not further revised in the light of more than twenty years subsequent experience in many countries. However, it is doubtful if further revision would have resulted in any drastic change in his views, as he held tenaci-ously to his opinions and upheld them in the face of all opposition. This marked independence of character had its obverse and reverse sides; it supplied the confidence and self-reliance desirable in an independent consultant, yet unfitted him for team work and collaboration. With very rare exceptions, petroleum geologists have entered the service of the oil companies, whose large staffs have provided opportunities for team work and for frequent consultation with colleagues. Cunningham Craig was cut

off from these advantages for the greater part of his career, and gradually became increasingly isolated, yet holding tenaciously to his opinions. Indeed, only gradually failing powers prevented this enterprising and intrepid Don Roberto from becoming the Don Quixote of petroleum geology.

Cunningham Craig suffered more than most consultants from the danger to which all are exposed. During boom periods, new companies are formed, and the less scrupulous promoters are tempted to include in their prospectuses brief extracts and sentences torn from their context and with qualifying considerations and clauses omitted. He inadvertently laid himself open to this treatment by his tendency to free and somewhat bold discussion of the prospects and possibilities of concessions.

Cunningham Craig's keenness for work was perhaps equalled by his zest for play. He was keen on riding, shooting, golf, fishing, tennis, billiards, bridge, etc., and his proficiency in these sports and games provided much justification for his own estimate of his prowess. A somewhat amiable trait was his exaggerated regard for whatever belonged to him ; for example, a horse or dog of his was inevitably the best for miles around. Another trait was his curious fondness for boomerangs, and the description by a stranger that he had seen " a geologist with a beard who was busy fashioning a boomerang " was unmistakable.

Some people there were who took too seriously his airy *obiter dicta* and failed to appreciate the somewhat stimulating and slightly acid viewpoints thus presented. For many months the writer of this note lived in the same bungalow with him, worked in the same office room, attended the same club, and lived and worked with him alone in the jungle. Throughout this close association he was interesting and stimulating, and an understanding, helpful and most considerate colleague.

In 1910 Cunningham Craig married Anna Irene, daughter of the late Rev. William Cleaver. There were no children, but otherwise the marriage was exceptionally happy.

In recent years, particularly during the war years, Cunningham Craig's powers began to fail. He had, during an active career in many lands, used up somewhat recklessly his abounding energy and vitality. Just over a year ago he slipped and fell down a darkened stone staircase, and received injuries from which he never fully recovered. Thus ended the career of a vital and unique pioneer of British petroleum geology, and those who knew him best will be the first to salute his passing and the last to retain memories of his characteristic qualities.

T. D.