PROBLEMS AND RESEARCH IN WATER FLOODING.*

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THE growing realization that our petroleum reserves are not inexhaustible and that a high engineering efficiency in operations usually means a high economic efficiency has stimulated research in petroleum production. While the budgets involved are relatively small as compared with those in petroleum refining, the expenditures are on the increase. One division of petroleum production which has been receiving considerable research attention is secondary recovery. This has followed from necessity, because of the numerous problems involved, the high operating cost, and the need for high operating efficiency in order to operate at a profit. This has been especially true in water-flooding, and it is the purpose of this discussion to point out some of the problems which have been studied in the research laboratory and to indicate some of the problems which are being, or will be, studied. The work will be considered in the order in which it might be encountered in the normal development of a waterflood property. Since the writer has had most of his experience in the Pennsylvania oil region, most of the examples cited will be from that area. However, it is felt that the majority of the work is sufficiently fundamental to have fairly general application.

One of the first operations performed in the development of an area for water-flooding is to drill some core wells for the purpose of sampling the formation to guide future work. The number of such wells will depend on the extent and the character of the area involved. The three principal coring methods used are: (1) rotary core-barrel, (2) cable-tool core barrel, and (3) chip coring.

The first two are fairly well-known methods, but the third has been used chiefly in Pennsylvania. It is a cable-tool coring method in which an ordinary cable-tool bit that has been dressed to a chisel edge is used.¹ Very short screws are drilled, and the cuttings, which vary in size from individual sand grains to pecan nuts, are removed by a sand pump. The larger cuttings or chips are used for analysis. Only one or two pails of water are used as the drilling fluid, which minimizes any flushing of the chips. The cable tool core-barrel requires sufficient water in the hole to cover the tools, which would give a head of water equivalent to about 20 lb. per square inch. If the formation pressure is less than this, there will be some penetration of drilling fluid. Since the rotary core barrel, requires that the drilling fluid be circulated, there will be a fairly high pressure on the formations being cored and, therefore, a maximum of flushing. Whilst the plastering effect of the drilling mud tends to reduce the flushing action, the extent is limited except in the cases where special

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additives have been used. If the formation being cored is under any appreciable pressure the cores will bleed when brought to the surface, which introduces another error.

It can be seen that one of the major problems in secondary recovery is an accurate sampling of the formations for a determination of fluid saturations. In areas where the average permeability is fairly low, core contamination may not be too serious. For example, in the Bradford Field in Pennsylvania, where the average permeability is of the order of five millidarcies, the three coring methods named are used successfully to predict behaviour. In higher permeability formations errors due to flushing are introduced. The various methods which have been used to minimize these difficulties are (1) the use of low loss additives to drilling muds, (2) pressure core barrels, (3) fluid tracers, and (4) combinations of these. While these represent improvements, they do not completely overcome the difficulties. For example, a method has been developed ² for differentiating between the connate, drilling, and flood-water in a core. While it labels the water present in the core sample at hand, it does not give the condition of the formation before the well was drilled.

In areas where there are available fairly accurate production figures, it is possible to obtain the fluid saturations by a material balance calculation assuming that the formation was originally 100 per cent. liquid saturated. The connate water saturation may be obtained from cores taken with an oil base mud, which assumes that the penetration of the oil does not displace any of the water. The connate water plus the produced oil (corrected for shrinkage) subtracted from the total pore volume gives the oil saturation in place. Another method for determining the connate water saturation was developed by Archie,³ in which the resistivity log and resistivity tests on brine saturated core samples are used. The difficulty with these methods is that they yield average values for the reservoir and do not indicate local variations.

In view of the importance of obtaining samples of the formation with a minimum of contamination, work is being performed on the problem. It is believed that one of the likely methods of attack is through the use of a very low loss drilling muds plus tracers.

While the actual fluid saturation of a formation may be in question because of sampling difficulties, it is generally felt that a laboratory is able to make a fairly accurate analysis of the sample at hand. In most cases this is true, but some cases have been brought to the attention of the writer in which the ordinary routine tests will not give the correct result. For example, let it be supposed that a producing formation contains some solid asphalt or paraffin along with the liquid crude oil at the formation temperature. Such a situation is possible in a shallow formation which was originally deeply buried, but over geological time the overburden has been eroded away bringing the formation closer to the surface. This would (1) reduce the temperature of the formation and (2) allow some of the gases which were dissolved in the crude oil under pressure to escape. Both of these factors would tend to precipitate a material such as paraffin wax, the first by a reduction in solubility and the second by a loss in solvent. In the case of asphalt, the situation would not be as clear cut, but the effect would be similar. A

determination of the oil saturation by the ordinary extraction or retort techniques will result in a value which is too high. What is wanted is the liquid oil saturation, since this is the quantity which will determine the recovery.

Research work is being done on the problem, and some core samples from one small pool which had a solid paraffin in it at the formation temperature had wax saturations up to around 6 per cent. One criterion for such a condition is that the cloud point of the crude should be very close to the formation temperature.

The routine determination of porosity and permeability on cores is fairly well established, but the interpretation of these quantities to field behaviour is one of the major problems in secondary recovery. Up to just recently, it has been supposed that the permeability measured with a gas such as air is identical with the single phase liquid permeability. Klinkenberg⁴ showed that this is not true, and found that the apparent permeability was a linear function of the reciprocal of the mean pressure. By extrapolating the line to infinite mean pressure, the liquid permeability is obtained. It is this liquid permeability which should be used in making calculations in water-flooding. The discrepancy between the air and liquid permeabilities is not serious in the high permeability range, but at low permeabilities the error may be greater than 100 per cent. In a series of permeability tests made on Bradford sand cores it was found that air permeabilities of 1, 10, and 100 millidarcies were about 87 per cent, 33 per cent, and 16 per cent greater respectively than the theoretical liquid permeabilities. The liquid permeabilities and relative permeability vs. saturation curves based upon the liquid permeability should be used to calculate water intake rates and rates of oil recovery in water-flooding.

If a rotary core has been taken, one of the advantages is that a flood recovery test can be made in the laboratory, providing that flushing by the drilling fluid is at a minimum. If flushing has been extensive, the remaining oil saturation is sometimes considered to be the residual to be attained after a normal water flood. Since it is sometimes difficult to determine the extent of flushing, it may not be a safe criterion to use for determining the lower limit of flooding. In some cases the core is extracted, saturated with brine, flooded with oil, and this artificially saturated core is then water-flooded. By extracting and resaturating the core, it is possible to study the recovery process under varying conditions. At the present time the data obtained from flooding virgin or artificially saturated cores have chiefly a qualitative application. One of the complicating factors is the possible presence of the so-called "end effect," which is the piling-up of liquid at the producing end of the core. Since the core samples are not large, it may have an appreciable effect upon the results. The effect is tied up with the relative wettability of the oil and water for the sand surface, and this is being studied along with the magnitude of the end effect. It is hoped that this research work will enable laboratories to measure both the residual oil saturations under different flooding conditions and the effective permeabilities of both oil and water at different saturations. For example, an important factor in water-flooding is the effect of pressure gradients on recoveries. This is controlled both by the effective flooding pressure and the spacing. Laboratory work has shown that

higher-pressure gradients usually result in greater ultimate recovery as well as an increased rate of recovery. This is supported to some extent by certain field results. However, the magnitude of the effect of pressure gradients on recoveries is not known too well, and, therefore, the effect of well spacing and flooding pressure cannot be evaluated accurately. Work is being done on this problem, and it is hoped that a fairly simple and rapid laboratory test will be developed for evaluating this factor.

The results of the core analyses should determine the well spacing, possibly the pattern of wells, method of well completion, and predict the water requirements and fluid production. At the present time the spacing is determined chiefly by the permeability of the formations. It is the general practice to attempt to flood out a property within ten years, and the spacing is accordingly increased for higher permeability sands. In an area which is badly broken or lensed, the increased spacing will result in a loss of oil which complicates a decision on spacing. The pattern in some cases is set by the location of old wells, but the five-spot seems to be favoured. More attention is being given at the present time to the effect of pattern on operating cost, flood-out time, cumulative water-oil ratios, and other factors. In a simplified analysis of the problem, a recent paper ⁵ points out that the seven-spot pattern has certain advantages in these respects.

If the producing formations have a heterogeneous permeability profile, the wells should be completed so as to take this into consideration. There are three methods which have been used in a development programme for correcting for variations in the permeability of strata. They are: (1) multiple packer completions, (2) delayed drilling, and (3) corrective shooting.

In the first method, the strata in the input wells are segregated into groups by multiple packer set-ups, and separate conduits carry the water down to these strata so that the flooding pressures may be varied on them.

The method is both troublesome and costly and is not used very much. Care must be exercised in shooting the wells, since the packer location cannot be fractured, and in some cases they cannot be shot at all, which gives low input rates. In the second method the input wells are drilled first and the water injected into all of them simultaneously in such a way that the oil is pushed to the centre of the individual patterns. This requires that the inputs be balanced carefully in order to have the oil concentrated at the location of the future producing well. By this method the lower permeabilities. When the rate of water input becomes slow, the producing wells are drilled and immediately begin to produce oil. There is a danger of by-passing oil in the tighter sections of the formation if a vertical movement is possible between strata. The water from a filled-up high permeability section can migrate into a lower permeability stratum ahead of its advancing oil-bank and block its progress to the producing well.

The third method of minimizing the disadvantages of a heterogeneous permeability profile—namely, by corrective shooting—requires that a heavier explosive charge or larger-diameter shell be placed opposite the low permeability strata rather than opposite the high permeability sections. This increases the effective radius of the well to different extents in the

125

various strata. Since the wells are the bottlenecks for fluids entering or leaving the formations, this technique will control the rate of fluid movement in the strata, and in the Bradford area permeability variations having a maximum ratio of about one to five can be shot to flood out at about the same time. With the 300-foot five-spots and $6\frac{1}{4}$ inch wells normally used in the Bradford area, a fifty and a ten millidarcy strata can be made to water out at about the same time by leaving the fifty millidarcy section unshot and shooting the ten millidarcy stratum with the maximum size shell.

In order to apply corrective shooting in an area, it is necessary to know (1) the shot responsiveness of the formation and (2) the extent of the effect needed. The first may be obtained by the analysis of field data in which the calculated effective well radii from water input rates are compared with the shot concentrations. The second is obtained from theoretical calculations on the time necessary to water out a sand using different effective well radii. The evaluation of the first factor requires a background of some experience in an area. It would be highly desirable to develop some laboratory test involving perhaps the tensile and compressive strengths and elasticity of the formation for predicting its shot responsiveness. A small amount of work has been done along these lines, but the problem is far from being solved.

If a condition of heterogeneous permeability is aggravated by the absence of impermeable horizontal breaks and the vertical migration of fluids is quite free, the techniques just mentioned will not be too successful and oil would be by-passed by a flood. In the circumstances, water-flooding might not be economically feasible, and secondary recovery by air-gas drive would be in order. Any oil which has been by-passed in waterflooding is extremely difficult to recover, but in the same situation in which a gas is the drive medium the oil is not lost but is usually produced slowly at high gas-oil ratios.

The production of the oil from a development may be by two different methods, (1) by pumping and (2) by flooding. In the second method a packer is set above the producing formation, the formation pressure is used to flow the oil and water to the surface, and the hydrostatic head in the input well is neutralized by an equivalent back pressure in the producing well. The rate of production by flowing will be slower than by pumping because of the lower gradients, but the operating cost will be much lower. Here again the question arises regarding the effect of pressure gradients on recovery. If higher pressure gradients are favourable, then flowing will result in some loss of oil. This may be more than outweighed by lower operating costs. There is one other factor which is unfavourable in flowing, and that is the counterflow of liquids away from the producing well into strata which have not begun to produce. If the counterflowing liquid is oil, its production will be deferred until the stratum "breaks" into the well. If the counterflowing fluid is water, some oil production may be lost because of the difficulty of pushing the water out with oil. It has been found that flowing can be used quite successfully as a salvage operation when the operating cost by pumping is just about equal to worth of the produced crude.⁶ Flowing under such conditions will lower operating costs sufficiently to prolong the economic life of the property.

Water for flooding operations is usually obtained from the most convenient lowest cost source. This may be fresh water, brine from a waterproducing stratum, or both. If a choice is possible it is sometimes advantageous to use brine, since laboratory studies and some field tests have indicated that the effective permeability may be higher than in the case of fresh water. This is chiefly due to the presence of such complex silicates as clay, which swell to a greater extent in the presence of fresh water than when in contact with brines. If a closed system is used in taking the brine from its source to the injection well, and oxygen is excluded, corrosion and treating costs will be at a minimum. With oxygen in the water, as is usually the case with fresh water or fresh water-brine mixtures, corrosion may be quite serious with a plugging of the formation by the corrosion products. Recently, increased attention has been given to the deaeration of flood water, and in one case, where sodium bisulphite has been used, very beneficial results were obtained.⁷

It was pointed out previously that it is not possible to correct variations in permeability completely by shooting if the span of permeabilities is too great. It would be highly desirable selectively to shut off or reduce the conductivity of the watered-out strata after they have produced their burden of oil, so as to reduce operating costs. Considerable work has been done both in the laboratory and the field on this problem.⁸ Colloidal dispersions such as special wax emulsions have shown excellent results in laboratory tests and a fair degree of success in the field. It should be pointed out that these compounds are permeability reducers, and not pluggers. All the strata have their permeability reduced somewhat, but the effect on the highest permeability strata is most marked. It is a filtration phenomenon in which the colloidal particles go to the formations in the same ratio as the quantity of water they take. Since this is greatest in the highest permeability, the plugging action is greatest there. The problem is not completely solved, however, and further work is in progress.

In the water-flooding area in Pennsylvania about one-third of the original oil in place was produced by gas expansion, about one-third more can be produced by present-day intensive water-flooding, and one-third remains in the reservoir. In many cases the residue represents more than onethird of the original oil. It would be in order to ask how this residual oil is held in the sand, and how at least a portion of it can be removed. In order to study these questions some synthetic consolidated oil sands in the form of thin slides made of sintered pyrex glass were used to study the problem microscopically. The flooding operation was observed under the microscope, and it was seen that the penetrating water took the easiest path in travelling through the sand, and by-passed small oil filled areas the access to which was by way of smaller capillaries. The residual oil was not in the form of thin films, as was postulated by some investigators. The process might be termed microscopic by-passing, as differentiated from macroscopic by-passing due to variations in permeability. This bypassing is caused by differences in capillary pressure along the paths of flow. Once a tiny island of oil has been by-passed, it is extremely difficult to remove. Theoretically, if the interfacial tension were made equal to zero, all the oil could be recovered, since it would be similar to extraction by a solvent. It follows, therefore, that chemicals which lower the interfacial tension between oil and water should increase recoveries. Laboratory tests have shown this to be true, but along with the advantages comes a decided disadvantage which has made it impossible to apply the method in the field as yet. The lowering of the surface or interfacial tension requires that the surface-active reagent be absorbed at such interfaces, and since extremely large areas of solid-liquid and liquid-liquid interfaces are present in the sand, the chemical is removed after the solution has penetrated a short distance. This results in two disadvantages—namely, that a large quantity of chemical is required, making it a costly process, and the drive medium at the flood front is water which is followed by an increasingly trailing solution of wetting agent. This latter process is very inefficient, in that a simple water-flood which has had the normal microscopic by-passing is followed by a wetting agent solution would be to have the wetting agent at the flood front.

Laboratory tests have shown that it is possible to reduce the residual oil saturation by about a half (from the one-third mentioned previously to one-sixth) in water-flooding if surface-active compounds are used. In the Bradford Field in Pennsylvania this would be an additional quantity of oil of the order of 110 barrels per acre foot. It would require about 5500 lb. of chemical to accomplish this. With oil at \$3.00 a barrel, the maximum possible price which could be paid for the chemical without incurring a financial loss would be six cents a pound. This is considerably below the present price of such chemicals. The hope is, however, that more efficient chemicals or more efficient methods of application will be found so as to bring this chemical flooding into an economic range.

The question is often raised as to the range of permeabilities which can be flooded. Laboratory work has been done on the lower limit, and it has been found that formations having permeabilities as low as 0.01 millidarcies and lower will be penetrated by the flooding pressures used in the field. However, the rate of penetration into such strata will depend on their effective permeability and the pressures involved. If the rate of flood advance is too slow, the oil bank will not reach the producing well during the economic life of the property. For conditions found in the Bradford Field, strata below 0.5 millidarcies are not considered in analyzing the behaviour of a property. This is a very arbitrary limit, however, since changes in conditions will cause it to vary. If the depth of the producing formation is fairly large, the maximum flooding pressure can be increased, and lower permeability strata will be economically floodable.

Experiments in the laboratory and some data from the field indicate that there is almost no upper limit in permeability for flooding. About the only obstacle would be a possible gravity separation of the oil and water in high-permeability sands. This would depend chiefly on the permeability, the thickness of the unbroken sand strata, and the flooding pressure gradients.

Since the flooding pressure is one of the most important of the controllable variables in a flooding operation, it is important to know its upper limit. A recent paper⁹ discusses the maximum flooding pressure, the effects when it is exceeded, and the criteria for its determination. From the analysis of field data and certain theoretical considerations it has been

128 YUSTER : PROBLEMS AND RESEARCH IN WATER FLOODING.

shown that the maximum safe pressure in pounds per square inch which can be applied on the sand face (not surface pressure) is about equal to the depth below the surface in feet. If there is 1000 feet of overburden, the maximum safe sand face pressure would be 1000 lb. per square inch. Pressures beyond this may exceed the downward pressure exerted by the overburden and part the formations, with a resultant by-passing action. Correcting for the hydrostatic head of water in the input well will give the maximum safe surface pressure as 0.57 times the thickness of the overburden. This theoretical criterion does not always hold, and a field test has been developed for determining the maximum pressure. A plot is made of the water input rate for a series of successively increasing or decreasing pressures. These rates should be taken as rapidly as possible. If sufficiently high pressures are available, the graph which is normally linear will show a break. The pressure at which the break takes place is the maximum safe pressure. Since the limiting factor is the downward pressure exerted by the overburden, there is a limit to the flooding rate of shallow and low permeability formations. This must be taken into consideration in the evaluation of such areas for water-flooding.

It can be seen from this brief outline that a large number of factors play a part in water-flooding operations. Some of them have been fairly completely solved, while others still require a great deal of attention. Their solution will come from both laboratory research and field studies, as has already been indicated.

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THE ESTIMATION OF THE SULPHUR CONTENT OF PETROLEUM DISTILLATES.*

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INTRODUCTION.

BECAUSE of the necessity for obtaining accurate results for the total sulphur content of benzine components, a series of investigations was undertaken to ascertain the accuracy of the "lamp method" of test, and to modify the apparatus employed, with a view to obtaining the desired degree of accuracy and sensitivity.

As a result of this work, a lamp was evolved which will give a very rapid and smokeless combustion of samples, including those with a high aromatic content. The results obtained with the apparatus finally adopted—a lamp for liquids, a burner for gases, a water-cooled chimney, and the absorber system—have been found to be accurate and reliable using gravimetric and turbidimetric methods for working up the test solutions.

Particular importance was attached to sulphur contents of less than 0.01 per cent. for which the existing volumetric methods were not suitable, though higher sulphur contents were not excluded from the investigation.

This apparatus, except for the larger size of lamp, has since been adopted, together with the methods of test, by the Institute of Petroleum, for inclusion as an extra standard method for sulphur determination. It will appear in the 1945 Edition of "Standard Methods for Testing Petroleum and its Products." Members may be interested to have an account of the reasons for its design and of the tests undertaken to ascertain the degree of accuracy obtainable with it.

In the first section of this paper is given an account of some preliminary work undertaken to ascertain the possibilities of a modified form of the gravimetric method I.P.T.-G.4. Descriptions are given of early alterations which were made to the gravimetric lamp to increase the rate at which samples could be burned, and of tests which were undertaken when this faster lamp was used.

This section also contains an account of tests which confirmed that a turbidimetric method published by Zahn¹ was suitable for sulphur contents lower than those catered for by the gravimetric method.

The next section deals with the final form of the fast-burning lamp, water-cooled chimney, and the absorber, and various matters connected with their use.

The final section gives the results of trial sulphur tests made with this apparatus to decide whether or not there was any loss of high-boiling sulphur compounds due to their retention on the wick of the lamp. Further objects were to measure the sulphur recovery if sulphur were present as carbon disulphide, and to decide upon the efficiency of a method for reducing errors in the sulphur recovery caused by the presence of tetraethyl lead in samples under test.

PRELIMINARY INVESTIGATION.

(a) The Gravimetric Method I.P.T.-G.4 (Modified).

For the early work results were obtained using the apparatus specified for the gravimetric method G.4 given in the I.P.T. "Standard Methods of Testing Petroleum and its Products," 2nd Edition (1929)—and a slightly modified form of procedure.

The modifications to I.P.T.-G.4 were :---

(i) Cotton wicking was used, as a satisfactory glass-wool was unobtainable at that date owing to the war situation.

(ii) The combustion of 10 ml. of sample in place of 5 ml.

(iii) The use of absolute ethyl alcohol in place of amyl acetate for ensuring the combustion of the last traces of sample.

(iv) Filtration of solution and washings from absorber prior to oxidation and precipitation. This filtration was carried out on the hot solutions.

(v) The analytical procedure used for working up the test solutions was that which is given in the appendix to this paper for use with gravimetric estimations.

(vi) A blank test was carried out burning 2 ml. of ethyl alcohol, air being allowed to pass through the blank apparatus for the same duration of time as for the sulphur determination.

This method was known from experience to be reliable, but, lacking published data, a check was made on solutions of pure ethyl sulphide in *iso*-octane. The sulphur content of the *iso*-octane (0.0002 per cent.) was determined by a turbidimetric method.¹

Known sulphur content, %-wt.	Oil burned, g-	Precipi- tate, g.	Precipi- tate less blank, g.	Deter- mined sulphur content, %-wt.	Average deter- mined sulphur content, %-wt.	Error, %-wt. of oil burnt.
Blank (1) (2)	nil nil	0.0003 0.0003			_	-
0.0013 (1) (2)	$6.972 \\ 7.539$	0.0007 0.0009	0·0004 0·0006	0·0008 0·0011	0.0010	-0·000 3
0.0057 (1) (2)	$6.863 \\ 7.745$	0·0029 0·0034	0·0026 0·0031	0·0052 0·0055	0.0054	-0.0003
0.0111 (1) (2)	6·747 6·783	0·0057 0·0055	0·0054 0·0052	0·0110 0·0105	0.0108	-0.0003
0·108 (1) (2)	7·930 8·794	0.0606 0.0675	0·0603 0·0672	0·105 0·105	0.105	-0.003

TABLE I. Trials of Gravimetric Method.

The results of this check are given in Table I, and show that over the range of sulphur contents 0.001-0.01 per cent. the error found was 0.0003 per cent., while at a sulphur content of 0.1 per cent. the error was 0.003 per cent. In view of the small weights of barium sulphate involved, it was considered that the errors found with the lower sulphur contents would often be exceeded, that the method was limited to sulphur contents down to 0.001 per cent. and that results should ordinarily be reported to the nearest 0.001 per cent.

(b) Initial Modification to the Lamp Used for I.P.T.-G.4.

The time required for the combustion of non-aromatic samples in the lamp specified for use with I.P.T.-G.4 was approximately 3-4 hours.



TEE-PIECE LAMP.

Highly aromatic materials required dilution with up to twice their volume of ethyl alcohol in order to obtain a smoke-free combustion. As it was still necessary to burn 10 ml. of sample to obtain an adequate order of accuracy in the sulphur content range under investigation, this meant that the total charge to the lamps was often 30 ml. which took 11–13 hours to burn.

An alteration was therefore made to the lamp specified for I.P.T.-G.4 by replacing the wick tube by a glass tee-piece and injecting approximately 0.1 little/minute of primary air into the wick tube below the level of the top of the wick. No opening or slit was permissible in the cork of the lamp for "breathing." Using this lamp, 10 ml. of even the most highly aromatic samples were completely burned in 2-3 hours without the necessity for dilution with a non-aromatic solvent. The only limitation to the rate of burning was the effect of the heat of the flame on the rubber joint between the chimney and absorber and a tendency for the absorber solution to evaporate. A diagram of the lamp is shown in Fig. 1.

Trial sulphur determinations made using this tee-piece lamp and the I.P.T.-G.4 lamp showed satisfactory agreement.

A more definite confirmation that high-boiling sulphur compounds are not concentrated on the wick of the tee-piece lamp was made by carrying out determinations on dilute solutions of gas-oil in *iso*-octane. Three sets of tests were made in which the gas-oil solution was followed up by burning two 2 ml. portions of ethyl alcohol, one 2 ml. portion of ethyl alcohol and no ethyl alcohol to clear the wick after the completion of the combustion of the sample. The sulphur content of the gas-oil-*iso*octane solutions was calculated from the sulphur content of the two components.

The sulphur content of the gas-oil component of the solution had been determined by the modified form of I.P.T.-G.4, burning approximately 2 gm. in ethyl alcohol using the G.4 lamp. Duplicate determinations giving the same result had been made by the bomb method using a procedure similar to that now given for I.P.-61/42. These two procedures have been demonstrated to give concordant results even with light lubricating oils, indicating that both methods probably give accurate results for true total sulphur content of gas-oils. The lamp method, burning more sample, gives greater precision.

The sulphur content of the *iso*-octane used for the gas-oil solution was shown to be less than 0.001 per cent. by the modified form of I.P.T.-G.4, using the I.P.T.-G.4 lamp. The value used for calculation purposes (0.0002 per cent.) was obtained by the turbidimetric procedure.¹

	Sulphur found, %-wt.								
Material burned.	"Slow "lamp. 2 alcohol washes.	Tee-piece lamp. 2 alcohol washes.	Tee-piece lamp. 1 alcohol wash.	Tee-piece lamp. No alcohol wash.					
Solution A.	$ \begin{array}{c} 0.103 \\ 0.104 \\ 0.100 \\ 0.101 \end{array} \right) \text{Average} \\ 0.102 \\ 0.101 \end{array} $	$\begin{array}{c} 0.103 \\ 0.104 \\ 0.099 \\ 0.099 \\ 0.009 \\ \end{array} A \text{ verage} \\ 0.101 \\ 0.099 \\ \end{array}$	$\begin{array}{c} 0.100\\ 0.105\\ 0.105\\ 0.100\\ 0.101 \end{array} $ A verage 0.102	$\begin{array}{c} 0.100\\ 0.098\\ 0.098\\ 0.106\\ 0.102 \end{array} $ A verage 0.102					
Solution B: calculated S content, 0 0108% (solu- tion A diluted with <i>iso</i> - octane).	0.010) Average 0.011 0.011	$\begin{array}{c} 0.009 \\ 0.009 \\ 0.010 \\ 0.010 \\ 0.011 \end{array} A verage$	$\begin{array}{c} 0.008\\ 0.009\\ 0.013\\ 0.010 \end{array} \right) \text{ Average } \\ 0.010\\ 0.010 \end{array}$	0.009 Average 0.006 0.008					
Solution C: calculated S content 0.0056% (solu- tion A diluted with iso- octane).	0.0057 Average 0.005 0.005	C	0.005 Average 0.003 0.004						
iso-Octane : sulphur con- tent, 0.0002% by turbidi- metric method.	<0.001) Average <0.001 <0.001	$\begin{array}{c} 0.001 \\ < 0.001 \end{array}$ Average $\begin{array}{c} 0.001 \\ < 0.001 \end{array}$	${}^{<0.001}_{<0.001}$ Average ${}^{<0.001}_{<0.001}$	$< 0.001 \\ 0.003 $ Average 0.002					

TABLE II.

Comparison of Gravimetric Sulphurs Determined with "Fast" and "Slow" Lamps. Solutions of Gas Oil in iso-Octane

The results obtained with the tee-piece lamps and the slow lamps given in Table II show that even with high-boiling sulphur compounds there is good agreement between the results obtained with both types of lamp, and that the sulphur contents obtained are close to the known values for the sulphur content of the materials burned. It is also apparent that there is very little loss of sulphur recovery due to the concentration of sulphur compounds on the wick of the fast lamp, even when the lamp is allowed to burn to dryness and the wick is not cleared by the combustion of a sulphur-free diluent.

(c) Turbidimetric Procedure (Zahn).

Simultaneously trials were made of the turbidimetric method due to Zahn,¹ in which the combustion is carried out in purified air. The method specified for working up the test solution is substantially the same as that given in the appendix to this paper. A very slightly modified form of the lamp, chimney, and absorber given by Zahn in his paper has since been adopted by the A.S.T.M. for their Method of Test D.90-41T.

Preliminary trials showed the method to be satisfactory for the work envisaged in the low-sulphur-content range, but to facilitate its operation, changes were shortly made in the apparatus as follows :----

The volumetric type of absorber was difficult to wash out into a beaker in preparation for working up the solution, so this was changed for the I.P.T.-G.4 type of absorber, which has a drain tube at the bottom.

The chimney described by Zahn has a capacity of only about 50 ml., the lamp therefore had to be inserted with some dexterity, in order to have it in place, and the secondary air-stream flowing, before the reserve of air was exhausted. This was therefore replaced by a spherical chimney of 700 ml. capacity, which gave a sufficient reserve of air to allow ample time for inserting the lamp.

Zahn's paper suggested the use of a Betz-Hellige instrument for turbidity measurements. No such instrument being available, a Baird and Tatlock photo-electric turbidimeter was successfully used in its place.

After these modifications had been made and a fair number of apparatus set up, a further series of trials was made using solutions of pure ethyl sulphide in *iso*-octane, over the range of sulphur contents 0.00020-0.0050per cent. The results of the trials of Zahn's method which are given in Table III confirmed that the turbidimetric procedure was suitable for sulphur contents lower than those which could be determined by the gravimetric procedure.

While these trials of the turbidimetric method were being carried out, it was noticed that a failure to use the sieved crystals of barium chloride specified by Zahn for the precipitation of sulphur as barium sulphate resulted in occasional erratic readings of the turbidimeter. It was also noticed that, owing to the different type of turbidimeter employed, the optimum volume of test solution was greater than that required for the Betz-Hellige for a given sensitivity (100 ml. in place of 50 ml.). There was a corresponding increase in the volume of alcohol-glycerol colloid stabilizer and in the precipitation time, both of which were doubled, becoming 20 ml. and 10 minutes, respectively.

	-							
A.	в.	C.	D.	E.	F.	G.	H .	I.
Material burned.	Sulphur content of material burned, %-	Weight burned, g.	Blank (electric). Milligr	Sample.	Sample, less blank. ulphur.	Sulphur found, %.	Average sulphur found, %.	Error, %.
i-Octane	0-00003	6·95 6·95 6·97 6·97	0 080 0 080 0·082 0·063	0.075 0.059 0.088 0.090	$-\frac{0.005}{-0.021} + 0.006 + 0.027$	$-\frac{0.00007}{-0.00030} + 0.00039 + 0.00039$	+0.00003	$\begin{array}{r} -0.00010 \\ -0.00033 \\ +0.00006 \\ +0.00036 \end{array}$
<i>i</i> -Octane + 0-00020% S.	0.00023	6·95 6·95	0.080 0.080	0·100 0·096	$^{+0.020}_{+0.016}$	$^{+0.00029}_{+0.00023}$	+0.00026	+0.00006 nil
i-Octane + 0.00040% S.	0·00043	6·92 6·92	0·091 0·081	$0.131 \\ 0.130$	$^{+0.040}_{+0.049}$	$^{+0.00058}_{+0.00071}$	+0.00064	$^{+0.00015}_{+0.00028}$
<i>i</i> -Octane + 0·00059% S.	0.00062	6·92 6·92	$0.091 \\ 0.081$	$0.150 \\ 0.160$	$^{+0.059}_{+0.079}$	$^{+0.00085}_{+0.00114}$	+0.00100	$^{+0.00023}_{+0.00052}$
<i>i</i> -Octane + 0·00197% S.	0.002	6·95 6·95	0·050 0·068	$0.184 \\ 0.213$	$^{+0.134}_{+0.145}$	+0.00193 + 0.00209	+0.00201	-0.00007 + 0.00009
<i>i</i> -Octane + 0·00492% S.	0 00495	6·97 6·97	0·082 0·063	0·424 0·373	+0.342 + 0.310	$^{+0.00491}_{+0.00445}$	+0.00468	

TABLE III. Sulphur Contents using Turbidimetric Method Due to Zahn.

The type of lamp used was a precurser of the type specified for A.S.T.M. D.90-41T. The burner was corked into the lamp flask instead of being fitted with a ground-glass joint, and great care had to be taken to avoid leakage of air and sample vapour through flaws in the cork.

(d) Conclusions Reached in Preliminary Work.

From the results already set out above, it was decided to use the turbidimetric procedure for all samples with a sulphur content in the range 0.0001-0.005 per cent. and the gravimetric procedure for those with a sulphur content above approximately 0.02 per cent. The intervening range can be covered equally well by both procedures. The existence of an upper limit for the turbidimetric procedure is caused by the opacity of the heavier precipitates of barium sulphate. Within limits this can be overcome by working with less sample, or by taking an aliquot portion of the test solution, but beyond a certain quantity of precipitate it is more accurate to make the measurement by weighing.

THE APPARATUS FINALLY ADOPTED.

The next stage in the work was to adapt the fast-burning lamp developed for gravimetric estimations, so that it could be used in an atmosphere of purified air and be used for both procedures of sulphur estimation. The turbidimetric method would then no longer suffer from the relatively long time spent in burning the sample, while the gravimetric method would be improved by carrying out the combustion in an atmosphere as clean as that used for the turbidimetric estimations.

This section deals with the final form of the lamp and apparatus, the rates of combustion of various liquid petroleum products in the lamp, the effect of the sulphur content of the wick, the purification and measurement of the air supplied to the lamps, the amount of heat evolved from the lamps, the method of carrying out the blank test and the effect of the presence of rubber in the apparatus on the results of sulphur tests.

(a) Lamp.

Experience with the Zahn apparatus showed that the lamp was not very much faster than the I.P.T.-G.4 type, and samples of high aromatic content required almost the same degree of dilution as with the I.P.T.-G.4



FIG. 2.

LAMP FOR LIQUIDS.

	Small.	Large.		Small.	Large.
A	69-71 mm.	69-71 mm.	I	7 mm. ext. diam,	7 mm. ext. diam.
в	46–50 mm.	46–50 mm.	J	6–10 mm.	6–10 mm.
C	29.5 - 30.5 mm.	29·5–30·5 mm.	K	10–18 mm.	10–18 mm.
D	38–42 mm.	38-42 mm.	\mathbf{L}	4.9-51 mm. int. diam.	$5\cdot 2-5\cdot 4$ mm. int. diam.
E	28-32 mm. •	28–32 mm.		6.7 mm. ext. diam.	8.0 mm. ext. diam.
F	approx. 40 mm.	approx. 40 mm.	M	10.5 mm. ext. diam.	12.0 mm. ext. diam.
G	14–18 mm.	14-18 mm.	N	3.9-4.1 mm. int. diam.	4.9-5 1 mm. int. diam.
H	1-2 mm.	1-2 mm			

The central wick tube is rounded off to form the slight constriction at N after the edges have been "trued."

The two parts of the wick tube must be in line and there must be no constriction at the joint with the main body of the lamp.

There must be no bulge at the joint X.

lamp. The primary air in the Zahn lamp passes through a tube concentric with the wick tube of the lamp, and is not mixed directly with the vapour of the sample. In order to take advantage of the greater sensitivity of the turbidimetric procedure and to measure sulphur contents down to 0.0001 per cent., it was still necessary to burn a minimum of 10 ml. of sample, though a smaller quantity of sample would have sufficed for sulphur contents above 0.01 per cent. Thus a considerable loss of time was involved in burning adequate quantities of material. It was therefore decided to apply the tee-piece type of lamp to the turbidimetric method. With the primary air injection at the optimum position in the wick tube, the simple tee-piece lamps cannot be corked into a chimney for use with purified air, because the tee joint interferes with the location of the cork. The design of the lamp was therefore changed to that shown as the small type of lamp in Fig. 2, in which the primary air is taken through a glass sleeve concentric with the wick tube, the injection then being made at the proper level through a division in the wick tube. The wick tube is made large enough to accommodate six lengths of standard cotton sulphur wick, this quantity being sufficient for the combustion of most motor fuels at a rate of 7–8 ml. per hour.



BURNER FOR GASES.

By slightly increasing the diameter of the wick tube to accommodate more wick, the rate of combustion of some volatile fuels has been increased to 24 ml. per hour, but the use of this large lamp for such fuels would necessitate an enlargement of the absorbing system, so its use has been restricted to the combustion of samples of kerosine, gas oil, and of alcohol for blank determinations. This is the large type of lamp shown in Fig. 2.

To prevent leakage of air and sample vapour through flaws in cork joints, the burner of the lamp and the sample flask are made as a unit, the only cork being in the filling tube at the side of the sample flask.

The wick is introduced by winding three turns for the smaller size of lamp and four for the larger size round a strip of wood 180 mm. long, which acts as a former, removing it from the former without cutting through the loops, and inserting the resulting six or eight lengths of wick through the filling tube into the sample flask. A hook-ended piece of wire is then pushed down the sample tube, engaged with the looped wick, and used to draw it up into the wick tube, so that 30-40 mm. project from the top. The loops are then cut through, and the strands of wick are combed parallel with each other. The wick is then drawn back into the tube and cut off square. Any excess of wick protruding from the filling tube is inserted into the flask. In the case of the smaller size of lamp used with some volatile aromatic samples a little less wick is required say five lengths instead of six. This is decided by experience.



- H	TG.	. 4.	
~			

	CHIMNEY.									
Α				105 mm.	G				140–160 mm.	
в				30 mm.	H				19.5 - 20.5 mm.	
С				25 mm.	I				18–22 mm.	
D				33 - 37 mm.	J				15-25 mm.	
\mathbf{E}		•		30-40 mm.	K				5–15 mm.	
\mathbf{F}				200-220 mm.	\mathbf{L}			-	9 mm.	

For very volatile samples, such as pentanes, the wick is drawn down to within 5 or 10 mm. of the division in the wick tube, and the wick tube above this level is plugged with a further piece of wick. This plug should consist of ten or twelve lengths of wick about 10 mm. long. The plug should not touch the main wick.

A suitable burner for gas samples is shown in Fig. 3. It consists of a simple heat-resistant glass tee piece plugged with cotton wick.

(b) Chimney.

The quantity of heat evolved from these lamps was sufficient to evaporate the absorber solutions and melt the rubber tubing by which the chimney was attached to the absorber. The chimney was therefore modified by fitting a water-jacket to the exit tube as shown in Fig. 4.

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(c) Absorber.

Though the absorber specified for use with I.P.T.-G.4 was satisfactory for use with these lamps and chimneys, it was found that the volume of water condensed from the products of combustion justified an increase in its diameter above the level of the glass beads. This increase in diameter





ABSORBER SYSTEM.

A			300 mm	H		25 mm.
в			120 mm.	I		35 mm.
C			20 mm.	J		25 mm.
D		-	140 mm.	K		9 mm.
E			3 0 mm.	\mathbf{L}		30 mm.
\mathbf{F}			140 mm.	\mathbf{M}		25 mm.
G			25 mm.			

gives greater freedom from the risk of "carry-over" of fluid from the absorber to the Drechsel bottle. The modified absorber is illustrated in Fig. 5.

(d) Blank Estimations.

For "blank estimations" on the air and reagents, parallel determinations can be made using alcohol to simulate the flame of the burning

139

sample, or an electric heater can be used in place of a flame to oxidize the sulphur impurities in the air. A suitable type of electric heater for corking into a chimney is shown in Fig. 6.





ELECTRICALLY HEATED ELEMENT FOR USE WITH BLANK DETERMINATIONS.

(e) Assembly.

A diagram of the assembled sulphur apparatus is shown in Fig. 7.

(f) Rates of Combustion.

Values for the rate of combustion of five petroleum products in fast lamps are given in Table IV, the time measured being that required for the charge in the lamp to burn to dryness under sulphur test conditions. These rates of combustion were considered to be sufficiently fast to enable a suitable quantity of the various materials to be burned in a sufficiently short period of time for the work in hand, so no further steps were taken to increase the rate of combustion, such as by the use of the large size of lamps for the more volatile samples coupled with the use of a large absorbing system, and the use of an even larger lamp for the less volatile samples.

(g) Sulphur Content of the Wick.

When a lamp is burned to dryness, a short length of wick is often con-The sulphur content of the wick was therefore measured turbidisumed.



FIG. 7. ASSEMBLY.

R	ate of Bu	erning of	Various	Material.	s in .	Fast L	amp	S.	
Material.		Dilu	Diluent.		Time to burn to dryness under sulphur test conditions,				Average rate of combustion
Nature.	Volume, ml.	Nature.	Volume, ml.	lamp.	Individuals.		Average.		sample, ml./hour.
iso-Octane.	20		nil	Small	Hrs. 2 2 2 2	Mins. 17 33 28 29	Hrs. 2	Mins. 27	8.2
Benzol.	20		nil	Small	22	23 45	2	34	7.8
SO ₁ extract from kerosine.	20		nil	Small	3 3 3 3	12 8 7 3	3	71	6.4
Kerosine (Pool).	10 10		nil nil	Small Large	2 1	$\begin{array}{c} 20 \\ 45 \end{array}$	2 1	20 45	4·3 5·7
Gas oil.	5 5	Alkylate	5 5	Small Large	42	0 40	4 2	0 40	1·25 1·9

 TABLE IV.

 Rate of Burning of Various Materials in Fast Lamos.

metrically after combustion in the bomb, a blank determination being made with a smaller length of wick. This came to 0.289 mg. per gram of wick. If 10 g. of a sample were burned for sulphur content, an increase in the sulphur recovery of 0.01 mg. due to the accidental combustion of a portion of the wick would increase the reported value for the sulphur content of the sample by 0.0001 per cent. From the above value of the sulphur content of the wick, the quantity of wick to be burned to produce this effect would be $\frac{0.01}{0.289}$ g. The total weight of wick ordinarily present in the type of lamp under consideration is of the order of 0.6 g., therefore it would be necessary to burn $\frac{0.01}{0.289} \times \frac{100}{0.6} = 6$ per cent. of the wick. This has a length of some 7 millimetres, and is a far larger quantity than is charred or burned in practice, so the effect of the combustion of a portion of the wick on the sulphur results obtained can therefore be considered as being negligible.

(h) Air Purification.

Owing to the difficulty of obtaining large quantities of purified air with a negligible sulphur content, it was decided to remove gross impurities by partial purification with a water scrubber, and to meter the quantity of air used by each lamp, all lamps, including the blank, being adjusted to consume the same quantity.

Several published methods for purifying the air supply for the lamps were tried. None of them gave air with a negligible sulphur content, and it seems that the efficiency of the method of purification is seriously affected by the nature of the sulphur bodies which it is necessary to remove. It was found that the simple procedure of scrubbing the air with a continuously renewed supply of tap-water was as efficient as any other process for removing gross contamination of the air of the laboratory where this work was carried out. On account of its simplicity and its suitability for handling large quantities of air, this method was finally adopted, and was used for most of the work described in this paper. In addition, it is safe, as there are no strong chemicals liable to blow out into the room if a breakage or leakage occurs.

As only partial purification had been achieved, it was necessary for all lamps, including the blank, to be set to consume the same quantity of air. When assessing air purity from sulphur blank estimations it is necessary to subtract the sulphur content of the reagents and distilled water which is often a large fraction of the total blank. On this account it is also necessary that during sulphur estimations all reagents must be used in measured quantities, and that the total volume of distilled water used should not be allowed to vary greatly from test to test.

Air purity is satisfactory for most low sulphur estimations if the quantity of air used during a test does not contribute more than 0.1 mg. sulphur to the blank.

At one refinery laboratory ordinarily showing 0.3-0.7 mg. of sulphur in the blank, satisfactory purification has been achieved by scrubbing the air with 95 per cent. sulphuric acid prior to further purification.

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It has been found that the supply of purified air available must be more than the bare minimum required to work the lamps, and that the purified air manifold by which it is distributed to the lamps must be large enough not to show an appreciable drop in pressure along its length. If these conditions are satisfied, the control of a large number of lamps presents no difficulties, but if they are not, then any adjustment made to the air supply to one lamp will effect the adjustment of all the others, and the system becomes very difficult to control.

(i) Volume of Air Consumed by the Lamps.

The sulphur lamps for use in a batch of tests are set to consume the same volume of air. A convenient rate for the fast lamps is about $2\cdot3-2\cdot5$ litres per minute (primary plus secondary). This is easily measured by fitting a flow-meter at the outlet end of each apparatus. The error caused by measuring the discharged air instead of the ingoing air is shown in the calculations summarized in Table V, which give the volume of air

TABLE V.

Theoretical	A ir	Requirements	and	Meter	Errors.
-------------	------	--------------	-----	-------	---------

	Burning 10 ml. per hour of the following							
	Ethyl alcohol.	Pentane.	Octane.	Hexa- decane.	Benzene.			
Total air required, litres/min Loss in volume of air after the	0.9	1.2	1.4	1.5	1.5			
meter reading, litres/min.	0.07	0.10	0.10	0.11	0.06			

theoretically required to burn 10 ml. per hour of various substances and the difference between that volume and the volume of air leaving the apparatus after water vapour has been condensed and carbon dioxide absorbed. The largest error in measurement calculated is 0.11 litre a minute for hexadecane. This error is too small to have any practical significance during a sulphur determination.

(j) Heat Evolved by Fast Lamp and Method for Determining Blank.

The quantity of heat evolved from the fast lamp is very high compared with the lamps previously in use, and it was therefore necessary to determine experimentally whether a corresponding amount of heat is required in the blank determination in order to oxidize any sulphur impurities present in the air supply.

Assuming that 8.2 ml. of motor spirit are burned per hour, the same quantity of heat will be evolved by the combustion of approximately 12.5 ml. of ethyl alcohol per hour or by an electric heater of approximately 70 watts capacity.

The large size of fast lamps consumes almost this required quantity of alcohol (10.55 ml./hr.), and is therefore suitable for blank estimations. A 70-watt heater was also prepared, but as a large part of the heat appeared to be lost by radiation, its size was increased to 108 watts. This was

still not quite large enough, but no further increase was made. It was operated at a medium red heat.

""Flue Gas" temperatures from the lamps were measured using a chimney without a water-jacket, the exit tube being cut off short and sealed into a tee piece, so that a thermometer could be inserted. The determined exit air temperatures are given in Table VI.

TABLE VI.

Exit Air Temperatures from Chimneys.

	Alcohol	Alcohol	<i>iso-</i> Octane	Électric
	in small	in large	in small	keater,
	fast lamp.	fast lamp.	fast lamp.	108 watt.
Average rate of burning, ml./hr. ,, total air, litres/min ,, inlet air temp., °C ,, exit air temp., °C ,, rise in air temp., °C	5·5 2·3 19·5 96·5 77	$ \begin{array}{r} 10.55 \\ 2.3 \\ 22.5 \\ 150.5 \\ 128 \end{array} $	$ \begin{array}{r} $	$ \begin{array}{r} 2\cdot 3 \\ 21 \\ 121 \cdot 5 \\ 100 \cdot 5 \end{array} $

A series of blank sulphur tests was then carried out simultaneously, using no heater or lamp, alcohol in a small fast lamp, alcohol in a large fast lamp and a 108-watt electric heater. These tests were carried out in duplicate on two successive occasions. The element in the electric heater was of nichrome wire. Previous tests had shown that there was no detectable advantage in using platinum. The results given in Table VII

TABLE VII. Blank Determinations.

		Duration	Weight of sulphur found.		
Method.	Batch No.	of test, hours.	Individuals, mg.	Average, mg.	
"Purified" air passing through apparatus but no flame or heater.	$\begin{array}{c}1\\1\\2\\2\end{array}$	3.28 3.28 3.67 3.67	0·104 0·084 0·111 0·087	0.097	
Ethyl alcobol burned in small fast lamp.	1 1 2 2	3·28 3·28 3·67 3·67	0·097 0·103 0·087 0·075	0.091	
Ethyl alcohol burned in large fast lamp.	1 1 2 2	3·28 3·28 3·67 3·67	0·097 0·097 0·100 0·074	0.092	
Electric heater (108 watts).	1 1 2 2	3·28 3·28 3·67 3·67	0.097 0.101 0.106 0.091	0.099	

show that the average blank is the same, within the limits of experimental error, for all methods. A part of the blank (usually about 50 per cent.)

comes from the reagents and distilled water which are measured, and therefore constant quantities.

From the above results it is evident that it made no difference whether a heater or flame was used or entirely omitted. The necessity for a heater or flame is probably a function of the nature of the impurities present at the time of test, and it was therefore considered advisable to retain its use. Preference was given to the electric heater, on account of ease of handling. In addition, ethyl alcohol or other low sulphur content material would have to be tested for that impurity prior to use.

(k) Effect of Rubber Tubing and Stoppers in the Absorber.

It was considered possible that sulphur dissolved from the rubber tubing and stoppers used in the absorber system might have an effect on the test results obtained with low-sulphur-content fuels. Comparative determinations made with rubber-free apparatus demonstrated that the quantity of sulphur absorbed from the rubber (red rubber) was too small to be detected in the results. The rubber-free apparatus was too inconvenient to be retained for routine use.

TRIAL SULPHUR CONTENT DETERMINATIONS WITH THE NEW APPARATUS.

(a) Methods of Test.

The methods of using the apparatus for samples in the gravimetric and turbidimetric ranges are given as an appendix to this paper. The gravimetric procedure is a modification of the Institute's Method I.P.T.-G.4, while the turbidimetric method is taken from that due to Zahn.¹ In connection with the latter, the absorbing solution has been changed from 30 ml. of a solution of 1 per cent. of bromine in 1 per cent. caustic soda to 20 ml. of N/4 sodium carbonate. Ten millimetres of 1 per cent, bromine in caustic soda are added to the washings from the absorbing system after the combustion has been completed. The reason for this change is that the carbon dioxide produced during the combustion of the sample was found to be sufficient to drive off all the bromine from the absorber solution during the first minute.

(b) Trials with Solutions of Gas Oil in iso-Octane.

Since evaporation of the sample takes place along the upper 30 mm. of wick in the fast lamp, it was necessary to use test samples which would demonstrate whether or not any of the heavy ends of the sample remained unburned on the wick. This point had already been satisfactorily cleared up over a sulphur content range up to 0.1 per cent. by the gravimetric method using the lamp shown in Fig. 1, so this new set of trials was confined to sulphur contents in the range below 0.006 per cent., using the turbidimetric method and the final form of the apparatus. Solutions of gas oil in *iso*-octane, prepared by diluting a master blend, were used for this purpose. The sulphur content of the master blend was determined by the gravimetric method (using a slow lamp) described at the beginning of this paper, the method having been shown to give accurate results for such solutions. The sulphur contents were calculated from the sulphur content of the master blend (0.1035 per cent. sulphur by weight) and the sulphur content of the *iso*-octane (0.00033 per cent. sulphur), which was determined turbidimetrically using the fast lamp apparatus.

Two sets of trials were carried out; in the first set 20 ml. of sample were burned to dryness and followed by 2 ml. of absolute ethyl alcohol (see Table VIII), and in the second set the lamps were burned to dryness

TABLE VIII.

Trial Sulphur Contents with Fast Burning Lamp—Turbidimetric Procedure. Charge Burned to Dryness Followed by 2 ml. Ethyl Alcohol.

Material burned.	Calcu- lated sulphur content, %.	Weight burned, g.	Blank (electric). Milligr	Sample.	Sample less blank. ulphur.	Sulphur found, %.	Average sulphur found, %.	Error, %.
iso-Octane.	0.00033	$14.00 \\ 14.00 \\ 14.00 \\ 14.00 \\ 14.00 $	0.097 0.101 0.106 0.091	$\begin{array}{c} 0.168 \\ 0.154 \\ 0.128 \\ 0.127 \end{array}$	0.071 0.053 0.022 0.036	0.00051 0.00038 0.00016 0.00026	0.00033	$ \begin{array}{c} + 0.00018 \\ + 0.00005 \\ - 0.00017 \\ - 0.00007 \end{array} $
iso-Octane + gas oil.	0.00075	$14.00 \\ 14.00$	0·087 0·078	0·177 0·189	0.090 0.111	0.00064 0.00078	0.00071	-0.00011 + 0.00003
Ditto.	0.00138	14·00 14·00	0·087 0·078	0-268 0-309	$0.181 \\ 0.231$	$0.00129 \\ 0.00165$	0.00147	-0.00009 + 0.00027
Ditto.	0 00243	$14.00 \\ 14.00$	0·064 0·104	0·435 0·443	$0.371 \\ 0.339$	0-00265 0-00242	0.00253	+0.00022 - 0.00001
Ditto.	0.00561	14·00 14·00	0·081 0·104	0·850 0·947	0·769 0·843	0-00549 0-00602	0.00556	$^{-0.00012}_{+0.00041}$

Average error (treating all as either positive or negative so that they shall not cancel) . 0.00014% Maximum error . . . 0.00041%

and the alcohol wash omitted, the weight of oil consumed being determined by weighing the lamps before and after burning (see Table IX).

TABLE IX.

Trial Sulphur Contents with Fast Burning Lamp—Turbidimetric Procedure. Charge Burned to Dryness but not Followed by Sulphur-free Solvent.

Material burned.	Calcu- lated sulphur content, %.	Weight burned, g.	Blank (electric). Milligra	Sample.	Sample less blank. ulphur.	Sulphur found, %.	Average sulphur found, %.	Error, %.
iso-Octane	0.00033	$13.387 \\ 13.504$	0.080 0.093	0·127 0·119	0.047 0.026	0.00035 0.00019	0.00027	+0.00002 - 0.00014
iso-Octane + gas oil.	0.00075	$13.435 \\ 13.377$	0·108 0·108	$0.204 \\ 0.255$	0·096 0·117	0.00072 0.00087	0.00079	-0.00003 + 0.00012
Ditto.	0.00138	13·587 13·366	0·080 0·093	$0.243 \\ 0.283$	0·163 0·190	0·00120 0·00142	0.00131	-0.00018 + 0.00004
Ditto.	0.00559	$13.511 \\ 13.445$	0·108 0·108	0.852 0.853	0·744 0·745	0·00551 0·00554	0.00553	-0.00008 - 0.00005

The average error of the first set of trials was ± 0.00014 per cent. weight with a maximum error of + 0.00041 per cent. The average error of the second set of trials was ± 0.00008 per cent. with a maximum of - 0.00018 per cent. This order of accuracy for sulphur contents in the range 0.0003-

0.006 per cent. was considered to be adequate. These results have been reported to the fifth place of decimals. For routine work there would be no justification for going beyond the fourth place.

(c) The Recovery of Sulphur Present as Carbon Disulphide.

It is known that sulphur present in samples as carbon disulphide is not fully accounted for when tests are carried out using the lamps specified for I.P.-62/41 and A.S.T.M. D90-34T. A blend of low-sulphur-content alkylate and carbon disulphide was accordingly prepared and tested by the gravimetric method with the slow lamp required for I.P.-62/41 and turbimetrically with the fast-lamp apparatus.

In order to prevent loss of CS_2 by evaporation, it was introduced into a tared glass ampoule with a capillary neck, sealed, and weighed. The ampoule was then crushed beneath the surface of the alkylate in a tared flask, which was then made up to volume and weighed. The master blend so prepared was further diluted with alkylate for test purposes. The sulphur content of the alkylate (0.0002 per cent.) was allowed for in calculating the sulphur content of the blend.

The results given in Table X show that a 100 per cent. recovery of the CS_2 sulphur was achieved using the fast lamp. The results obtained with

Type of lamp used.	Sulphur found, %-wt.	Average sulphur found, %-wt.	Actual sulphur present, %-wt.	Recovery, %-wt.
Slow lamp.	0.0188 0.0180 0.0182 0.0194	0.0186	0.0229	81
Fast lamp	0.0226 0.0228 0.0234	0.0229	0.0229	100

TABLE X. Sulphur Content of Alkylate Containing Sulphur as Carbon Disulphide.

the slow lamp confirm the published figures for the low recovery of CS_2 sulphur with this lamp.

(d) The Effect of Tetraethyl Lead on Sulphur Test Results.

It had been noted that the presence of tetraethyl lead in samples caused the results obtained for total sulphur content to be too low for high sulphur contents and too high with very low sulphur contents, working with fast or slow lamps, gravimetric or turbidimetric procedure.

An attempt was made to reduce this error by removing the greater part of the lead from the sample by shaking it with one-fifth of its volume of cold fuming hydrochloric acid (38-40 per cent. w/w). The sample was then washed with water before being measured for the sulphur determination.

A large number of tests were made using fuels of different types to examine the effect of T.E.L., total sulphur content being determined



before and after the addition of lead fluid, and also after its removal by the acid-wash procedure given above.

These results, which are presented graphically in Fig. 8 and in tabular form in Table XI, show that the effect of tetraethyl lead on the sulphur test results is more marked in the case of tests carried out with the fast lamp than with the slow lamp. In either case the effect is quite large, and it can be largely overcome by washing the lead out of the sample with cold fuming hydrochloric acid.

The author desires to thank the Directors of The Anglo-Iranian Oil Co.,

TABLE XI.

Sample.	Clear leaded or deleaded.	Lamp used.	Number of determinations made and method.	Average indicated sulphur content, %-wt.	Error.*
	Close	Fost	5 Turbidimetric	0.0001	nil
A	Clear	Slow	4	0.0001	nil
	Leaded	Fast	10	0.0002	+0.0001
	Loadeou	Slow	4	0.0005	+0.0004
	Deleaded	Fast	5	0.0001	nil
	Deremanda	1 4000			
в	Clear	Fast	5 ,,	0.0007	nil
		Slow	4	0.0008	+0.0001
	Leaded	Fast	7 ,,	0.0004	-0.0003
	15	Slow	4 ,,	0.0009	+0.0002
	Deleaded	Fast	4 ,,	0.0007	nil
		_			
-	Clear _	Fast	4 ,,	0.0039	nil
С -		Slow	5 ,,	0.0034	0.0005
	Leaded	Fast	10 ,,	0.0019	-0.0020
	D ¹ 1 1	Slow	4 "	0.0024	-0.0015
	Deleaded	rast	4 ,,	0.0094	-0.0000
ъ	Cloan	Fort	3 Gravimetrie	0.005	nil
D	Olear	Slow	2	0.005	nil
	Leaded	Fast	2	0.0015	-0.0035
	Lioudou	Slow	2	0.003	-0.002
	, ,,		_ ,,		
E	Clear	Fast	4 ,	0.0085	-0.0012
	15	Slow	2 ,.	0.010	nil
	Leaded	Fast	2 ,.	0.004	-0.006
	22	Slow	2 ,	0.008	-0.002
				0.1097	**
F	Clear	Slow	2 ,	0.1035	nil
	Leaded	Slow	2 ,,	0.0975	-0.006
	1				

Effect of T.E.L. on Total Sulphur Determinations.

* Sulphur content of clear sample in fast lamp taken as correct for turbidimetric estimations and clear sample in slow lamp for gravimetric.

Ltd., for permission to publish this paper and Dr. D. A. Howes for the encouragement given during the course of the work.

Reference.

¹ V. Zahn, Industrial and Engineering Chemistry, 1937, 9, 543.

APPENDIX.

THE USE OF THE APPARATUS FOR SULPHUR CONTENTS BY THE TURBIDIMETRIC AND GRAVIMETRIC METHODS.

The manner of using the apparatus and working up the test solutions by gravimetric and turbidimetric procedures is summarized in the following paragraphs.

QUANTITY OF SAMPLE AND CHOICE OF METHOD.

If the sulphur content of the material being examined is less than 0.005 per cent. weight it is desirable to burn a minimum of 20 ml. of sample. The test solution obtained by washing out the apparatus at the end of the combustion is worked up by the turbidimetric method.

If the sulphur content is above 0.005 per cent. and less than about 0.02 per cent., the quantity of sample burned can be reduced, if desired, to about 10 ml., and the test solution worked up by either the turbidimetric or the gravimetric procedure. If the turbidimetric procedure is used, it may be necessary to work with only an aliquot portion of the test solution.

With sulphur contents above 0.02 per cent. it is usual to burn 10 ml. of sample and work up the test solution by the gravimetric method.

Clear gas-oils not containing appreciable quantities of asphaltic material can be burned if diluted with a volatile solvent of low sulphur content. Light petroleum distillates or alkylates are preferable to alcohols as solvents for this purpose. The advantage of the lamp method over the bomb method is particularly noticeable with gas-oils of low sulphur content, the lamp enabling more sample to be burned and a higher order of accuracy to be obtained than is possible with a bomb of conventional size. In order not to flood the wick with undiluted gas oil, the diluent is measured in first and then a suitable volume, say 5 ml. of the sample, is weighed in.

Gum deposition in the wick from spirit samples containing gum can be prevented by diluting the sample with secondary butyl-alcohol.

If a spirit sample contains lead tetraethyl, it should be washed with fuming hydrochloric acid till lead free before being taken for sulphur determination. A satisfactory procedure is given in the text of this paper.

REAGENTS.

Only analytical reagent chemicals of the best quality should be used for preparing the following reagents.

(a) For the Turbidimetric Method.

The following reagents are required for the turbidimetric procedure.

(1) N/4 aqueous sodium carbonate solution.

(2) Bromine in caustic soda solution. 1 per cent. by weight of bromine dissolved in 1 per cent. aqueous caustic soda solution.

(3) Normal hydrochloric acid.

(4) 20 per cent. aqueous caustic soda solution.

(5) Phenolphthalein.

(6) Alcohol-glycerol solution. This is a solution of one part by volume of glycerol in two parts by volume of ethyl alcohol. The alcohol need not be anhydrous, but it must be free from traces of undesirable impurities, including traces of hydrocarbons, which cause a turbidity to be produced when the alcohol-glycerol is mixed with the test solution.

(7) Barium chloride. Barium chloride crystals (BaCl₂,2H₂O) shall

be sieved, the fraction held on 30 mesh and passing 20 mesh being retained for use.

(8) Acid sodium chloride solution. This is a normal solution of sodium chloride containing 200 ml. of normal hydrochloric acid per litre.

(9) Standard sodium sulphate solutions. An aqueous solution of sodium sulphate shall be prepared. A convenient strength is such that 1 litre contains 1 g. of sulphur. This shall be checked gravimetrically. This solution forms a stock from which dilute solutions can be prepared for standardizing the turbidimeter. A convenient dilution is 0.02 mg. sulphur per ml.

(10) Distilled water. The distilled water used for turbidimetric sulphur determinations must be free from sulphate caused by "carry over" from the still.

(b) For the Gravimetric Method.

The following reagents are required for the gravimetric procedure :---

(1) 10 per cent. sodium carbonate solution. 100 g. anhydrous sodium carbonate dissolved in water and made up to 1 litre.

(2) Bromine water. A saturated solution of bromine in distilled water.

(3) Dilute hydrochloric acid. Concentrated hydrochloric acid diluted with an equal volume of distilled water.

(4) Barium chloride solution. 100 g. of barium chloride crystals $(BaCl_2, 2H_2O)$ dissolved in distilled water and made up to 1 litre.

(5) Indicator. Methyl orange, B.D.H.4-5 indicator, or other indicator of similar pH range.

PREPARATION OF THE APPARATUS.

The apparatus is assembled as shown in Fig. 7.

If the turbidimetric method of test is to be employed, the absorber is charged with 20 ml. of N/4 aqueous sodium carbonate solution, and a few drops of the same solution are placed in the Drechsel bottle and made up to about 30 ml. with distilled water.

If the gravimetric method of test is to be employed, the absorbent is 10 per cent. aqueous sodium carbonate solution. The same volume is used as was required for the turbidimetric procedure.

The wick used for the lamps and for the gas burners is of the same type and quality as that specified for I.P.62/41. The method of inserting it in the lamps is given in the text of the paper.

As a safety precaution, when burning gas samples, the chimney should be surrounded with a piece of stout wire gauze.

LIGHTING AND CONTROL OF THE LAMPS.

All the lamps are inserted into the chimneys, and the secondary air is turned on to a volume of approximately 2.0 litres per minute for each lamp.

The cooling water is turned on.

The lamps are removed and lighted one by one. If several lamps are taken out at the same time, there may be an excessive drop in the pressure of the purified air in the manifold. The primary air is turned on just prior to lighting the lamp, the wick being lowered if necessary by tapping the lamp. The lamp is then re-inserted in the chimney and the rubber band is rolled down over the cork joint. Further adjustments are made to the wick when required by tapping the lamp while in position in the chimney.

If the correct amounts of primary and secondary air have been turned on, the lamp is not extinguished when inserted into the chimney. If the wick has been properly trimmed, the flame will be uniform, resembling a bunsen flame with a luminous tip. There is no flickering.

The normal total air requirement per lamp is $2 \cdot 0 - 2 \cdot 5$ litres/minute. The quantity of primary air required varies with the type of fuel burnt; it is generally about 0.3 litres/minute, and is adjusted so as to give a steady smokeless flame which is not pierced by jets of unburned vapour and air mixture. It is not necessary to obtain a non-luminous flame.

All the lamps, including the blank, are set to consume the same total volume of air.

The lamp is burned to dryness, and this is followed by the combustion of 2 ml. of absolute ethyl alcohol to consume the portion of sample remaining on the wick and in the lamp. Alternatively, if the sample was weighed into the lamp, the alcohol wash may be omitted and the empty lamp weighed at the end of the test. It is probably satisfactory to burn only a part of the charge in the lamp, determining the quantity consumed by the loss in weight of the lamp, but insufficient trials have been made to date to justify as yet the adoption of that procedure with this type of lamp. Those trials already made have given accurate results.

If both gravimetric and turbidimetric determinations are being made simultaneously, separate blanks should be run for each, as the blank test measures not only the sulphur impurities in the air used for the combustion, but also sulphur impurities in the reagents. The blank tests can be carried out either by burning absolute ethyl alcohol in a lamp or by using an electrically heated element to replace the flame. A suitable element is shown in Fig. 6.

If the sulphur content of a gas sample is being determined, it is essential that the sample should be fed to the burner at a steady pressure of a few inches of water. A fluctuating gas pressure will cause the burner to go out.

WORKING UP THE TEST SOLUTIONS-TURBIDIMETRIC PROCEDURE.

The contents of the absorber and Drechsel and the inner surface of the chimney are washed into a beaker. 10 ml. of the 1 per cent. bromine in caustic soda solution are added followed by 15 ml. of the normal hydrochloric acid. The liquid is then evaporated to a volume of approximately 50 ml. or less. The extent of the evaporation required is governed by the make of turbidimeter used. A few drops of phenolphthalein are added, and the solution is made just alkaline with the 20 per cent. caustic soda. The solution is then exactly neutralized with the N/1 hydrochloric acid, after which an excess of 3.0 ml. of N/1 acid is added. If a number of samples is being tested it is convenient to add the standard acid from a 100-ml. burette.

The acidified solution is filtered cold through a retentive filter paper, such as a 12.5-cm. Whatman No. 44, into a graduated Nessler jar and made up to a standardized volume. If a Baird and Tatlock photoelectric turbidimeter is being used, this standardized volume can conveniently be 100 ml.

The contents of the Nessler jar are mixed, using a stirring rod, and transferred to the turbidimeter cell. 20 ml. of the alcohol-glycerol solution is added and stirred in by means of a rubber-tipped stirring rod. If the standardized volume of test solution is different from 100 ml., the volume of alcohol-glycerol solution can be changed proportionally. Air bubbles are allowed to clear, and the initial turbidity is measured. Approximately 0.3 g. of the barium chloride crystals are added by means of a standardized dipper, and stirred in with the rubber-tipped stirring rod until completely dissolved. This usually takes about half a minute, but it is better to standardize on a time such as one minute. After the lapse of ten minutes the final turbidity of the test solution is measured. Before reading the turbidity (initial or final) it is necessary to examine the sides of the test cell. If air bubbles are found, they must be removed. If the standardized volume of test solution is less than 100 ml. before adding the alcohol-glycerol solution, a shorter time can be allowed before reading the final turbidity. If the volume is 50 ml., five minutes usually suffices. If the volume is greater than 100 ml., a longer time is necessary.

The weight of sulphur precipitated as barium sulphate is deduced from the calibration curve of the turbidimeter. The weight of sulphur present in the blank is subtracted prior to calculating the sulphur content of the sample. The percentage of sulphur found in the sample is reported to the nearest unit in the fourth place of decimals up to 0.0099 per cent. and to the nearest unit in the third place for greater sulphur contents.

The turbidimeter is calibrated as follows. 15 ml. of the standard acid salt solution are measured into a Nessler jar, and an appropriate volume of the standard sodium sulphate solution is added. The whole is made up with distilled water to the standardized volume chosen for use with the turbidimeter, transferred to the turbidimeter cell, alcohol-glycerol is added, and the turbidity measured. The standardizing solution is then precipitated with barium chloride and the turbidity again measured, following the procedure used for the test solutions. A blank determination is made with the reagents and distilled water without any addition of standard sodium sulphate. A graph is then prepared showing the change of turbidity against weight of sulphur. The range 0-1.00 mg. is usually sufficient. It should be possible to read the graph to the nearest 0.001 mg. sulphur.

WORKING UP THE TEST SOLUTIONS-GRAVIMETRIC PROCEDURE.

The contents of the absorber and Drechsel and the inner surface of the chimney are washed into a beaker. The contents of this beaker are filtered into another beaker (this filtration may be accelerated by filtering the solution after heating to boiling), and 10 ml. of the bromine water followed by 10 ml. of the dilute hydrochloric acid are added to the filtrate. The filtrate is heated to boiling to expel the bromine, and a drop of the indicator solution is added. If the liquid does not show an acid reaction, sufficient extra acid is added.

10 ml. of the barium chloride solution are added slowly, the liquid not being allowed to cease boiling during the addition. Boiling is continued for a minimum of thirty minutes after the addition of the barium chloride. The contents of the beaker are then allowed to stand for a minimum period of six hours, and preferably overnight, after which the barium sulphate precipitate is filtered off, washed, and ignited using the usual analytical procedure. The sulphur content of the sample is calculated from the weight of barium sulphate less the weight of barium sulphate obtained from the blank estimation. The percentage of sulphur found in the sample is reported to the nearest unit in the third place of decimals, excepting when the sulphur content is 1 per cent. or above, when the sulphur content is reported to the second place of decimals.

SOME OBSERVATIONS ON THE MECHANISM OF THE DEVELOPMENT OF EXTREME PRESSURE LUBRICATING PROPERTIES BY REACTIVE SULPHUR IN MINERAL OILS.*

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SUMMARY.

Mineral oils containing free sulphur or active sulphur compounds possess extreme-pressure (E.P.) lubricating properties not shown by straight mineral oils. It has been suggested that the development of these properties is due to the formation of sulphide films on the metal surfaces which prevent metal-to-metal contact.

Sulphide films were formed on the surfaces of steel balls subjected to test in the Four-Ball Extreme-Pressure Lubricant Testing Apparatus. E.P. properties were observed using these treated balls, and a straight mineraloil lubricant, similar to those obtained using untreated balls and an oilcontaining reactive sulphur. The friction/time curves obtained using the treated balls show preliminary "sulphur curves" followed by "straight mineral-oil curves" as the sulphide film is worn away. The results, although somewhat irregular, offer some confirmation of the "sulphide layer" theory.

EXPERIMENTAL.

OLS containing free sulphur or reactive sulphur compounds show very typical friction/time curves when tested in the Four-Ball Apparatus (see Fig. 1). These curves indicate that no seizure—*i.e.*, metal-to-metal contact—occurs with these oils during test. In testing such oils black stains are frequently produced about the wear spots on the test balls, particularly at high loads, and it has been suggested that these stains are due to the formation of sulphide layers under the conditions of test.

Accordingly, sulphide films were formed on the steel surfaces of the balls for test in two ways :---

(1) By heating the balls, washed free from oil, in molten sulphurand removing the excess sulphur by heating and quenching in water. This gave very irregular coatings of sulphide.

(2) By washing the oil-free balls with dilute (ca. 5 per cent.) acid, then immersing them in ammonium sulphide solution, followed by drying at 100° C. This gave a thin, but regular sulphide film.

Untreated balls were first tested using Penna 150 Neutral Oil as lubricant. The treated balls were then tested using the same oil as lubricant. The results are tabulated below, the short duration (60 secs.) test—*i.e.*, the performance during one complete revolution of the recording drum being used throughout. (A full description of the Four-Ball Apparatus and Method of Test is given by D. Clayton, *Institution of Mechanical Engineers, General Discussion on Lubrication*, 1937, 2, 274).

Load (kgs.).	Mean Wear Diameter (mms.).	Occur- rence of Seizure (secs.).	Duration of Seizure (secs.).	Torque at Seizure.	Coefficient of Friction 1.		Remarks		
					Before Seizure.	After Seizure.			
		Unt	reated Balls	in Penna 1	150 Neutral.				
70	1.96	2.6	16.5	>0.25	0 03	0.12	Irregular wear.		
102	>3.5	0.5	28	>0.25 >0.25	0.04	0-10	53 59		
	(Slight welding)								
	Balls Treated in Molten Sulphur.								
70	0.70	27	8.0	0.10	0 03	0.07	Regular wear.		
102	1.95	13.0	16	0 13	0 06	0.04	77 73		
119	0.80	6.6	• 5·0 7·0	0.04	0.07	0.09	Tanogular Ween		
170	2.98	<0.2	30	>0.25	0.06	0.15	Integular wear.		
Repeat 270	Welding								
270	Welding								
Repeat									
Balls Treated with Acid Wash and Ammonium Sulphide.									
70	1.92	26	14.5	0.24	0.05	0 04	Smooth wear.		
102	2.33	3.3	25.5	>0.25	0.05	0.12	friegular wear.		





FIG. 5. WEAR/LOAD DIAGRAM.



DAVEY : DEVELOPMENT OF EXTREME

156



PRESSURE LUBRICATING PROPERTIES.

157

DISCUSSION OF RESULTS AND CONCLUSIONS.

The results obtained, though somewhat irregular in the case of the balls treated with molten sulphur, indicate that sulphide films produced on the balls yield very similar results to those obtained from oils containing active sulphur. It should be noted that the sulphide layer imparts load-bearing capacity to a straight mineral oil and gives a sulphur type of curve until the film is worn away, wear being produced on the balls after the sulphide layer has been worn away by the frictional forces.

It would appear, therefore, that the development of E.P. properties by oils containing active sulphur is due to the formation of sulphide layers on metal surfaces.

ACKNOWLEDGMENT.

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