The Cause of the Characteristic Odour of Shale Oil and Methods of Eliminating It

by

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INTRODUCTION.

The Scottish Shale Oil Industry, established by the late Dr. James Young, has for many years produced various grades of oil which, so far as their essential properties are concerned, are equal to the corresponding products from high class petroleums. The oils from shale are readily distinguished from the petroleum oils by their characteristic, somewhat unpleasant odour, which is more evident in the more volatile fractions, and this odour has affected their value and marketability. The experiments described in this Thesis have been carried out with the object of determining the cause of the characteristic odour of the burning oil fraction, and of devising methods for its removal.

"Burning oil" is that particular portion of hydrocarbon oil which distils mainly between 150 and 275°C. and has a specific gravity of about 0·80. The method at present in use in Scotland of producing this refined oil from the crude oil obtained by the distillation of shale is briefly as follows:-

The crude oil on distillation yields various distillates, all of which except the first (i.e. the crude naphtha), are mixed and subjected to treatment with concentrated sulphuric acid and caustic soda solutions. The acid treatment consists of agitation with 2·4% (by volume) of acid tar from previous treatments, plus 0·75% concentrated sulphuric acid specific gravity 1·84. A second acid treatment with 0·63% acid follows. The oil is washed with a caustic soda solution of specific gravity 1·35, and then distilled with steam,yielding (1) crude burning oil (2) heavy oil and paraffin (3) residuum. The crude burning oil is subjected to a further acid (0·67% by volume) and soda wash (0·75%), and again distilled with steam,yielding finally the refined burning oil. The yield of burning oil is from three to four gallons per ton of shale.

SUMMARY.

PART I.

The first really systematic investigation into the cause of the unpleasant smell of burning oil was carried out by Crooks of the Scottish Shale Oil Scientific & Industrial Research Association under the direction of Professor Thomas Gray. A brief summary of these experiments is given (pp. 1-7). Crooks concluded that the smell of the oil was due to the presence of certain sulphur bodies. A short, but fairly complete, account of the sulphur compounds which have been identified in mineral oil follows (pp. 8-12). The principal methods which have been in use from time to time of removing these are indicated (pp.13-21) particular attention being directed to Dunstan's hypochlorite process for refining petroleum distillates, which has proved to be the most successful of recent years.

PART II.

While Crooks did not actually isolate any individual sulphur body, his work left little doubt that the main cause of the unpleasant smell was compounds of the thioether class. Arrangements were therefore made to prepare such a compound synthetically, and study its behaviour towards (a) substances which form additive compounds with thioethers - metallic chlorides (b) materials capable of

selectively adsorbing sulphur bodies - bauxite and floridin (c) oxidising agents.

The thioether examined was isoamyl sulphide which, having a boiling point of 212°C., distills within the distillation range of burning oil, 150-275°C.

(a) Of the metallic chlorides only mercuric chloride completely destroyed the smell of the sulphide, due to the formation of the odourless crystalline compound $(C_5H_{11})_2S$ 2 $HgCl_2$. However, the solubility of the mercuric chloride, and to a less extent, the addition compound, in the oil rendered the process impracticable industrially.

(b) "White Rose" paraffin, to which the alkyl sulphide had been added, was filtered through a column of the bauxite or floridin. By this treatment, the colour of the oil was improved, the unpleasant smell was not so strong, while part of the thioether added was removed (pp. 33 and 34). To completely extract the thioether, however, the comparatively large quantity of material necessary was too great to offer much prospect of success.

(c) The oxidising agents, hydrogen peroxide, chromic acid, and sodium hypochlorite, in the cold, oxidised isoamyl sulphide to the corresponding sulphoxide or sulphone. Both these products are neutral, and are not removed by soda treatment, while on distillation they decompose into evil smelling products. Any oxidising treatment, therefore, must be such that subsequent distillation treatment is not necessary.

In view of the possible employment of oxidising agents it was necessary to consider the effect of such agents on unsaturated hydrocarbons, as shale oil contains 40% of these bodies. Amylene, diamylene and triamylene were prepared, and their tendency to oxidise when treated in the cold with solutions of potassium dichromate and hydrogen peroxide investigated (pp. 35-40). The results obtained demonstrated that, in the cold, dilute solutions of these reagents attack the above unsaturated hydrocarbons very slightly, and that such a treatment of burning oil would result in a negligible loss.

Two oxidising treatments of burning oil were carried out (1) with a 10% acid solution of potassium dichromate (pp. 41 and 42), and (2) with sodium hypochlorite solution of strength 0·3 N containing 0·7-0·8 grammes of caustic soda per litre (pp. 42-46). These treatments improved the smell of the oil considerably, but the colour of the product was adversely affected.

On distilling the treated oil a sharp, unpleasant odour was generated. A subsequent filtration of the oil through bauxite gave a product of satisfactory colour.

The hypochlorite treated oil gave slightly better results, especially as regards colour. The character of the oil, as indicated by the distillation range, specific gravity, and iodine number, showed no change. Tests for hydroxyl groups yielded negative results, while in the hypochlorite treated oil a trace of chlorine, 0·02%, was found. Thus, a possible method of deodorising the oil consists of an oxidising treatment, followed by filtration through bauxite.

PART III.

In the above processes it will be noticed that the sulphur is not removed from the oil - merely oxidised. A method of attack whereby, if carried far enough, the sulphur could be entirely eliminated, resulted from attempts to hydrogenate the oil. Briefly, the process consists of passing the oil vapour with hydrogen over finely divided nickel deposited on pumice stone at 300°C. This method of desulphurising hydrocarbon oil is not novel, although it was believed to be so when first suggested: E.V. Evans made a somewhat similar process the subject of a patent which will be referred to later. A sample of burning oil, partially desulphurised by filtration through bauxite (S = 0·086%), when treated in this way gave a water-white oil with a pleasant smell, an iodine number of 21, and of sulphur content 0·007%. On repeated treatment, an oil of iodine number 3·7 was obtained (p. 52). A similar experiment where 1,000 cc. of oil (S = 0·148%) not previously treated with bauxite were passed with hydrogen over the cata lyst in portions of 100 cc. each, gave distillates containing from 0·028% S in the first 100 cc. to 0·077% in the last 100 cc. (p. 53). The smell of the oil was pleasant and the colour, though not water-white, was better than that of the untreated oil. Copper (p. 54) and iron (p. 55) as substitutes for nickel gave comparatively poor results.

Experiments wherein the oil vapour was brought into contact with finely divided metals without hydrogen in a similar manner gave much less satisfactory products (pp. 58-60), and again nickel was more efficient than copper or iron.

A study of the decomposition of isoamyl sulphide, a typical open chain compound, and of thiophene, a ring compound, when vaporised and passed over finely divided metals, both alone and in the presence of hydrogen, is recorded (pp. 62-65). Using nickel as catalyst, isoamyl sulphide is decomposed into isoamylene and hydrogen sulphide. If hydrogen is present, part of the isoamylene is hydrogenated, giving pentane. The presence of hydrogen considerably assists in destroying the thioether, due, as is shown later, to the reduction of the higher sulphides of nickel. Iron in place of nickel was less efficient, while lime proved to be of little use.

Thiophene at 300°C. was little affected by the above treatment using a nickel catalyst, but at 500°C. 15% of the thiophene was attacked, yielding hydrogen sulphide and, presumably, butadiene, which by hydrogenation gave a quantity of butane (pp. 65-67).

The deodorisation of burning oil by passing the oil vapour with hydrogen over nickel at 300°C. was then taken up on a larger scale. A preliminary run gave unsatisfactory results. The smell of the oil was improved, but the amount of sulphur removed fell short of that eliminated with the smaller apparatus (pp. 68-72). Several reasons for this drop in the efficiency of the process were considered and investigated with the result that the subsequent experiments led to the following conclusions:-

1. The catalyst is equally active whether prepared from the oxide obtained by igniting the nitrate, or from the hydroxide formed by the action of caustic soda on a nickel nitrate solution.

2. The amount of sulphur removed from the oil is not increased by increaseing the temperature of the experiment to 400°C., or by increasing the proportion of hydrogen to oil vapour above 13 parts per 100 parts.

3. A greater proportion of the sulphur compounds, however, is destroyed if the size of the pumice is reduced, and a still further proportion is attacked when the ratio of nickel to pumice is increased.

In the last experiment of this series 19 gallons of burning oil were treated (pp. 81-84). The size of the pumice stone carrier and the ratio of nickel to pumice were the same as in the small scale experiment. The results obtained were not quite so good as in the latter case, but were satisfactory. It was demonstrated that the unpleasant smell of the burning oil was due to a small proportion of sulphur compounds (0·025% S), and that these compounds were readily decomposed by the above treatment. Evidence was obtained that the sulphide of nickel itself acted catalytically in bringing about the destruction of these bodies.

This view was supported by the behaviour of isoamyl sulphide and thiophene when mixed with hydrogen and passed over nickel subsulphide at 300°C. (pp. 90-93). The former decomposed into isoamylene and hydrogen sulphide, while the latter remained unchanged. The hydrogen sulphide generated reacted with the subsulphide to give higher sulphides, which were subsequently reduced by hydrogen. A study of the sulphides of nickel and their reduction (pp. 93-98) demonstrated that at 300°C. (1) hydrogen sulphide converts metallic nickel or the oxide to the tetrasulphide Ni_3S_4, (2) this sulphide is reduced by hydrogen to the subsulphide Ni_3S_2, but not to the metal, (3) if a mixture of hydrogen sulphide and hydrogen containing less than 2 parts of hydrogen sulphide per 1,000 parts hydrogen, the product formed by passing the mixture over either metallic nickel or its sulphides, is the subsulphide.

In considering the decomposition of the alkyl sulphide by a nickel subsulphide catalyst, it follows that catalytic action depends on the alternate formation of the higher sulphides of nickel and their reduction, thus -

(1) $(C_5H_{11})_2S = 2\,C_5H_{10} + H_2S$

(2) $Ni_3S_2 + H_2S = 3\,NiS + H_2$ and $3\,NiS + H_2S = Ni_3S_4 + H_2$

(3) $Ni_3S_4 + H_2 = 3\,NiS + H_2S$ and $3\,NiS + H_2 = Ni_3S_2 + H_2S$

As a result of these experiments, it appears that the open chain sulphur compounds are desulphurised by hydrogen in the presence of nickel or its subsulphide, while the more stable ring compounds are unattacked. Consequently, it may be presumed that the unpleasant smell of the burning oil is a property of the small percentage of these open chain bodies it contains. Since the subsulphide of nickel acts as a catalyst in decomposing these compounds, and since hydrogen containing not more than 2 parts of hydrogen sulphide per 1,000 parts of hydrogen reduces the higher sulphides of nickel to the subsulphide, a process which affords reasonable prospects of successfully deodorising the oil may be outlined as follows:-

The burning oil vapour from the final distillation is drawn with hydrogen through a chamber containing nickel deposited on pumice, or other carrier, maintained at a temperature of 300°C. The oil is condensed and collected as usual, while the excess hydrogen is passed through hydrogen sulphide purifiers to a gasholder and then re-circulated. By adjusting the rate of flow of hydrogen so that the concentration of hydrogen sulphide in the reaction chamber does not exceed 2 parts per 1,000 parts hydrogen, the deodorisation of the oil should proceed continuously.

PART I.

Summary of Crooks' work on the deodorisation of burning oil.

Many attempts have been made to destroy the peculiar smell of 'Scotch' burning oil, but these have met with little success. Most of these efforts, however, have been spasmodic, and no definite records of them remain. The first really systematic attack on this subject was carried out by Crooks of the Scottish Shale Oil Scientific and Industrial Research Association under the direction of Professor Gray. Since their results have not been published, and since the investigation recorded hereafter is based on the preliminary work of Crooks, I am indebted to Professor Gray and this worker for permission to give a brief summary of it here.

When this investigation started, opinion differed as to the cause of the smell of shale oil, but it was generally believed to be due to sulphur compounds, as in petroleum, or to unsaturated hydrocarbons. The preliminary experiments, therefore, consisted in treating the burning oil with various reagents, many of which have been utilised in deodorising petroleum, and noting the smell, sulphur content, and degree of unsaturation as indicated by the iodine number of the product.

The materials thus employed may be divided into three groups:-

I. Substances which unite with sulphur or sulphur compounds.

II. Substances which remove sulphur compounds by adsorption.

III. Oxidizing agents.

Tables I, II and III give details of the method employed and the nature of the product. Of the reagents used in Group I experiments the most efficient desulphurising agent was anhydrous aluminium chloride, but the product of this treatment had a sharp pungent odour. The characteristic smell of the oil was destroyed. The sharp odour later proved to be due to moisture in the oil and was not evident when the oil was dried over sodium wire before being subjected to the treatment. Unfortunately, however, considerable polymerisation of the unsaturated hydrocarbons, as indicated by the reduction of the iodine number from 73·2 to 7·5, took place, thereby resulting in a loss of 28-32% of the oil.

The most noteworthy result was that obtained by a mercuric chloride treatment (Table I, experiments 9 and 10) where, while only a small proportion of the sulphur was removed, the objectionable odour of the oil was destroyed and the iodine number unchanged. Subsequent experiments showed that a disadvantage of this treatment was the solubility of mercuric chloride in the oil, viz: 0·31 gms. per litre. All other Group I reagents improved the smell of the oil and sulphur content slightly, but the distinctive odour was still present.

In Group II experiments the oil was both agitated with and filtered through materials known to possess the property of selectively adsorbing sulphur compounds, such as alumina, bauxite, floridin and silica gel. As shown in Table II, these efforts met with only partial success. In each case the sulphur content of the oil was partly reduced, but its characteristic smell was not completely destroyed. The colour of the product, however, was much better than that of the original sample.

The effect of oxidising agents (Table III) was to reduce the sulphur content of the oil slightly, but its smell was not much improved. The smell of the product was better before the final distillation: the colour, however, was bad even after distillation.

TABLE I.

Unless otherwise stated 100 cc. of the oil were heated with the reagent under reflux for one hour and distilled to 270°C

	Reagent and the amount	Vol.of oil recovered cc.	Sulphur %	Iodine No.	Smell
1.	2 gms. Precipitated Lead	91	0·108		slightly improved
2.	5 " Copper Turnings	99	0·118	75·5	do.
3.	5 " Lead Dioxide	90	0·114		do.
4.	5 " Copper Oxide	91	0·121		do.
5.	5 " Copper Nitrate	82	0·109		smell of oxides of nitrogen
6.	5 " Lead Acetate	94	0·119		improved
7.	5 " Lead Resinate	87	0·122		no difference
8.	5 " Anhydrous Aluminium Chloride	72	0·049	7·5	
9.	5 " Mercuric Chloride in 50 cc. Ether	75	0·114	74·8	very good
10.	Mercuric Chloride	92	0·114		do.
11.	Stannic Chloride		0·112		slightly improved
12.	Ferric Chloride		0·107		do.
13.	Cuprous Chloride		0·111		do.
14.	Alcoholic Potash	83	0·127	72·95	do.
	Oil as received		0·134	73·2	

In experiments 10, 11, 12 and 13 the oil was filtered thro' the reagent.

TABLE II.

Two series of experiments were carried out -

A. - 100 cc. of the oil were agitated with the material for one hour.

B. - 100 cc. of the oil were filtered through a column of the material 16" high and of diam. $\frac{1}{2}$".

	Material and amount used.	Vol. of oil	Sulphur %	Iodine No.	Smell
A.					
1.	10 gms. Floridin (fine powder)	83	0·129	73·6	fairly good
2.	7 gms. Alumina (freshly ignited)	71	0·134	73·1	good
3.	10 gms. Bauxite	85	0·137	75·4	fairly good
4.	10 gms. Floridin (coarser than in 1)	80	0·134	74·8	good
B.					
1.	**Floridin (coarse A. 4)**	79	0·133	74·6	fairly good
2.	**Bauxite**	83	0·135	75·1	do.
3.	Silica gel 40 gms. **Activated at 320°C**	95	0·139	95·9	do.
	Untreated oil		0·134	74·2	

NOTE:- In B.3 the sulphur content and iodine number of the oil before treatment were 0·155% and 96·6.

TABLE III.

Unless otherwise stated 100 cc. of the oil were agitated in the cold with a solution of the oxidising agent. The product was then filtered, washed and distilled to 270°C.

	Oxidising Agent	Vol. of oil recovered cc.	Sulphur %	Iodine No.	Smell
1.	Acid Potassium Permanganate (heated on water bath)	87	0·115	73·9	fairly good
2.	Acid Potassium Permanganate (in the cold)	82	0·083	66·9	do.
3.	Alkaline Potassium Permanganate	80	0·127	74·8	do.
4.	Hydrogen Peroxide containing HCl not distilled	90	0·136	73·2	good
5.	**Lead Dioxide made into a paste with acetic acid**	82	0·129	82·0	fairly good
6.	**Acid Potassium Dichromate**	76	0·059	64·5	good
7.	**Sodium Peroxide (excess of dilute acid added)**	74	0·126	73·4	do.
	Original oil		0·130	75·5	

A consideration of these preliminary experiments led to the conclusion that the unpleasant smell of the burning oil was possibly due to the presence of mercaptans, thioethers and similar bodies - the affinity of such bodies for forming additive compounds with mercuric chloride being well known. On this assumption an attempt was made to isolate these odoriferous compounds by agitating 14 gallons of burning oil with powdered mercuric chloride, and subsequently decomposing these mercury compounds after the manner of Maybery and Smith. (1). An oil containing 3·29% sulphur was obtained, but no individual sulphur compound was isolated.

This concludes Crooks' work.

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Sulphur Compounds in Petroleum.

Since a review of Crooks' work indicated that sulphur compounds and not unsaturated hydrocarbons were the cause of the unpleasant smell in shale oil, it might be of advantage at this point to give a short outline of the work already done in the removal of sulphur and its compounds from petroleum. In this field it has been proved that sulphur bodies are the cause of the objectionable smell that most crude oils possess. In addition, some of these compounds have corrosive properties and may tend to oxidise and develop acidity, so that it has been necessary to eliminate them as far as is economically possible. To this end, the volume of work already published is considerable, but it is in the patent literature that a true conception of the progress of this work is obtained.

The nature of the sulphur compounds found in crude petroleum varies very much; some are easily attacked while others are destroyed only with the greatest difficulty. Below are given particulars of sulphur and sulphur bodies which have actually been isolated from petroleum.

<u>Free sulphur</u> has been identified in the crude petroleum of Texas by Richardson and Wallace (2) as well as in Californian oils by Peckmann (3), and in Roumanian oils by Bourquoi (4). According to Kraemar and Spilker (5)

the presence of sulphur is due to the activity of certain bacteria contemporaneous with the algae which this author regards as the source of petroleum.

Hydrogen sulphide. The natural gas accompanying petroleum rich in sulphur is usually rich in hydrogen sulphide. Further, in addition to the gas dissolved in the oil, a certain amount is produced during distillation by the decomposition of the more unstable sulphur bodies, and again, sulphur reacts with hydrocarbons to form hydrogen sulphide.

Mercaptans. These occur in distillates from Baku oil(6) and have lately been isolated from Persian "once run distillate" by Birch and Norris (7). Mercaptans are slightly acidic bodies, soluble in strong caustic soda solution, but are hydrolised on dilution, or on heating the dilute solution of the mercaptide. The acidity of the mercaptans decreases with increase in molecular weight. Mercuric chloride forms a crystalline mercapti- chloride with mercaptans of the constitution $R.S.HgCl$.

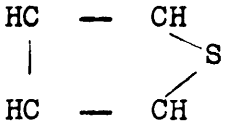
Mercaptides of the following metals have been prepared sodium, arsenic, antimony, bismuth, tin and cadmium(8).

Alkyl sulphides. Members of this series have been extracted from Ohio crudes by Maybery and Smith (1). These

These authors claim to have isolated methyl-, ethyl-, isobutyl-, pentyl-, and hexyl-sulphides. Kast and Lagai (9), however, state that these thioethers are not present in Ohio oil.. Charitschkoff (10) detected alkyl sulphides in naphtha from Grosny. The alkyl sulphides form white crystalline addition compounds with mercuric chloride. They are oxidised by mild oxidising agents to the sulphoxides, and by more drastic agents to the sulphones.

Alkyl disulphides. While the disulphides have been isolated by Birch and Norris (11) from the lighter portion of Persian "once run distillate", these authors hold the view that it is quite possible that these compounds are not present in the crude oil, but have been formed by the oxidation of the mercaptans during the distillation of the spent soda from which they isolated the mercaptans. Reference is made to the work of Holmberg (12) who states that alkali mercaptides in aqueous solution react with free sulphur or alkali polysulphides to give disulphides. Also Wendt and Diggs (13) found that diethyl disulphide is formed by the action of sulphur on ethyl mercaptan.

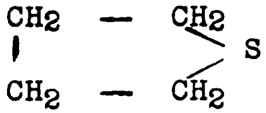
Thiophenes



and its homologues

Thiophenes have been found in Russian and German oils and recently in Kimmeridge shale oil (16). In connection with the presence of thiophenes and their possible mode of formation in hydrocarbon oil, it is of interest to note the work of Meyer and Nansen (17) and of Friedmann (18). The former found that thiophene is obtained in small quantities when a mixture of benzine and petroleum vapour is passed over strongly ignited iron pyrites, while the latter produced a thiophane $C_8H_{12}S$ and a thiophene C_8H_8S by heating octane in a sealed tube with sulphur. Steinkopf (19) observed that when acetylene was passed over heated pyrites thiophenes were obtained, and that butadiene in a similar way generated methyl thiophene. Henry (20) considers that thiophenes are formed by the combination of sulphur, or sulphur compounds, with unsaturated hydrocarbons. Thiophene and its homologues are a very stable class of compounds. They form, with mercuric chloride, compounds of the type: C_4H_3S HgCl but not so readily as the alkyl sulphides (21).

Thiophanes.

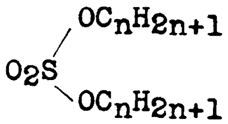


These bodies may be considered as saturated thiophenes or naphthene sulphides. Maybery and Quayle (22) have

have isolated these from Canadian petroleum. They react with bromine, but are not unsaturated, hydrogen bromide being liberated during the reaction. Oxidation of thiophanes with alkaline permanganate yield the corresponding sulphones (23).

Carbon bisulphide. Alkyl derivatives of carbon bisulphide are stated to be found in Canadian petroleum by Hager (24), and by Maybery and Smith

Alkyl sulphates.



$O_2S(OC_nH_{2n+1})_2$

According to Vohl (25) and Heusler and Dennstedt (26) and (27), alkyl sulphates are formed when oils are treated with sulphuric acid by union of the unsaturated hydrocarbons with the acid. Such esters are not readily removed from the oil by washing with alkali, and it has been noted that oils containing these esters yield on distillation considerable quamtities of sulphur dioxide, even after a heavy alkali wash.

Methods of removing Sulphur from Hydrocarbon Oils.

As regards the commercial application of desulphurising agents, many patents have appeared, but only a few have been widely adopted. A fairly complete list of patents on this subject is to be found at the end of this Thesis, while the more important ones will be described here. From the discussion of sulphur compounds found in petroleum and their nature,,it is seen that the removal of hydrogen sulphide and mercaptans is comparatively simple. The remainder, however, thioethers, disulphides, thiophenes etc. present a difficult problem.

Sulphuric acid process.

The method of refining petroleum originally used, and still in operation in many refineries, is to give the oil an acid treatment (1% by volume of concentrated sulphuric acid) followed by 1% by volume of oleum (20% SO_3) with subsequent washing with 30% caustic soda solution, and finally distilling.

Wood, Lowry and Faragher (28) state that sulphuric acid (sp. gr. 1·84) partially dissolves alkyl sulphides, and completely removes thiophenes; mercaptans are oxidised to disulphides, while carbon disulphide is unattacked. Anfibogoff (29) holds that the alkyl sulphides are insoluble in sulphuric acid, but Thole (30) found ethyl and methyl sulphide to dissolve "perfectly and readily" in 95-96% sulphuric acid. Heavy treatments with sulphuric acid cause polymerisation of the unsaturated hydrocarbons, resulting in a substantial loss. Again, alkyl esters are readily formed with the unsaturated hydrocarbons, and these are very difficult to get rid of.

Sodium plumbite process.

This process, which met with a considerable measure of success, consisted in agitating the oil with a sodium plumbite solution, allowing the mixture to separate, and drawing off the clear oil. A convenient strength of sodium plumbite solution is:-

15 parts by weight	litharge
15 " " "	caustic soda
100 " " "	water

The caustic soda is dissolved in water, heated, and to the boiling solution the litharge gradually added, each portion being dissolved before a further addition is made, the resulting solution being quite clear. On agitating the oil with this solution the action commences immediately, a blac precipitate being formed. The colour of the precipitate changes from yellow through red to black. Wendt and Diggs (13) attributed this to the formation of the alkyl lead mercaptides, and the subsequent interaction of the mercaptides with free sulphur (if no free sulphur is present in the oil flowers of sulphur are added) with the formation of lead sulphide and alkyl disulphides. The latter redissolves in the oil so that while the oil is considerably "sweetened" its sulphur content is not reduced.

On continued agitation of the mixture of oil and sodium plumbite the colloidal compounds coagulate, and then the mixture separates quickly. Addition of flowers of sulphur assists this separation. Watermann and Sissingh (31) show that while the oil is "sweetened" by the treatment of some hydrocarbon oils with sodium plumbite and flowers of sulphur, the actual sulphur content of the treated oil is greater than that of the original oil. On redistilling such a refined oil, considerable quantities of hydrogen sulphide were given off, and the sulphur content was reduced in one case from 1·3% to 0·42%. The net result of the sodium plumbite treatment is the conversion of the evil smelling mercaptans to the less odoriferous disulphides, and the removal of hydrogen sulphide while the thioethers, alkyl disulphides, thiophenes, and carbon disulphide derivatives are unattacked (Wood, Lowry and Faragher (28).

Frasch process.

Among the best known and most successful processes is that of Frasch (32). In this process the oil is distilled with a mixture of two or more oxides of the following metals copper, lead, iron, nickel, cobalt, cadmium, tin, antimony, bismuth, silver and mercury. One combination which has given satisfactory results is 75 parts of copper oxide, 10 parts of lead oxide and 15 parts of iron oxide. The mixture of oil and the above is kept in suspension, either by mechanical agitation, or by passing in steam and the whole slowly distilled. The desulphurised oil is distilled off, the sludge allowed to settle, and the oil containing a quantity of the oxides in suspension is added to the next charge. The residue is filtered off and regenerated by roasting. This method has been successful in desulphurising many oils, notably Canadian "skunk" oils, but a few, Mexican oils in particular, do not respond to this treatment.

Again the sulphur compounds eliminated are mercaptans and hydrogen sulphide, little effect being noted in carbon disulphide, alkyl sulphides and disulphides, thiophenes and free sulphur (28). Frasch also devised a process whereby the oil is treated in an autoclave, using a pressure sufficient to keep the oil liquid, although heated above its boiling point.

Edeleanu process (33).

The principle underlying this process is the solution of sulphur compounds in liquid sulphur dioxide. Petroleum distillates are mixed with liquid sulphur dioxide at a temperature of 50°C. Two layers separate out, the lower layer contains the unsaturated hydrocarbons and most of the sulphur compounds, while in the top layer are found the saturated hydrocarbons of the methane and naphthene series. Edeleanu found that the sulphur in a Mexican crude oil was reduced from 0·404% to 0·114% by this treatment, while the sulphur in oil dissolved in liquid sulphur dioxide after freeing from this gas was 1·10%. A Roumanian lamp oil of sulphur content 0·052% after treatment with liquid sulphur dioxide contained 0·008% sulphur. Unfortunately, this process is totally unsuitable for oils containing a large quantity of unsaturated hydrocarbons, particularly shale oils. According to Thole (30) liquid sulphur dioxide dissolves readily carbon disulphide, ethyl sulphide, ethyl mercaptan and ethyl disulphide.

Hall (34) proposes to remove sulphur from shale oil by distilling the oil in presence of sulphur dioxide and subsequently subjecting the oil to the Frasch treatment.

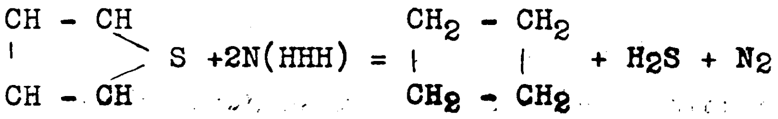
Walkey and Bargate (35) attain the same object by vaporising the oil in presence of steam and gaseous sulphur dioxide.

Ammonia process.

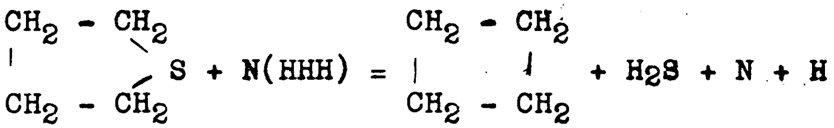
Lucas, Palmer and Perkin (36) have devised a method whereby the oil is treated with ammonia at high temperatures. The oil may be either liquid or gaseous. In the former case the pressure must be sufficiently high to prevent the oil vaporising, and the temperature must be high enough to dissociate the ammonia. The sulphur is removed as hydrogen sulphide.

Perkin, in his communication, gives three examples as to the possible mechanism of the reaction:-

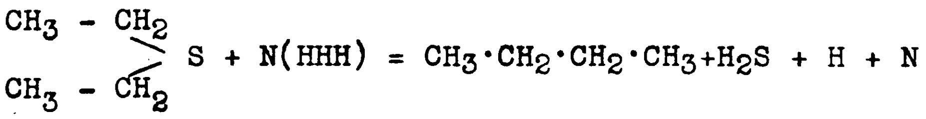
Thiophenes.



Thiophanes.



Alkyl sulphides.



The excess hydrogen Perkin considers will help to saturate any unsaturated hydrocarbons.

Glancy (37) eliminates sulphur compounds from petroleum by extraction with liquid ammonia.

Oxidation methods.

Many methods employing oxidising agents have been proposed, but only one seems to have passed into commercial use. This is the process successfully worked out by Dr. Dunstan (38) for treating Anglo-Persian distillates. According to this author the "once run distillate", i.e. the gasoline and kerosene fraction, is agitated with 10% of a 0·3N sodium hypochlorite solution containing from ½ to 1 gramme of free caustic soda per litre. This treatment is preceded, and followed, by a wash of 3% of a 10% solution of caustic soda. The gasoline is distilled off, while the residue containing the kerosene, or burning oil fraction, is filtered through bauxite in the proportion of 2 lbs. per gallon of oil. The activity of the hypochlorite depends on the amount of free caustic alkali present in the solution, and it is necessary to confine the free alkali to the narrow limits specified. Below the lower figure the hypochlorite is unduly unstable, while above the higher limit the activity of the oxidising agent becomes greatly reduced

In this connection it is interesting to note a patent by Thole and Card (39) in which the hypochlorite solution is rendered more active by treating the mixture of hypochlorite and oil with a current of carbon dioxide, or by adding to the mixture just before, or during, agitation, salts such as iron, manganese, magnesium or zinc sulphates. These salts react with the free alkali to form insoluble hydroxides, thereby rendering the hypochlorite more active.

Dunstan, in this same communication, gives the example of refining Anglo-Persian distillate by this method, reproduced below:-

Once run distillate (Sp. gr. 0·750
(Sulphur 0·15%
(Colour "Prime white"

Initial soda wash

1st Hypochlorite wash

2nd Hypochlorite wash

Final soda wash

Redistillation

Finished benzine (No. 1 spirit)

Sp. gr. 0·729

Sulphur 0·01%

Chlorine 0·01%

Kerosene residue

Filtration thro' bauxite

Finished kerosene

Sulphur	0·06 - 0·10%
Chlorine	0·01%
Colour	"Water white"
Sp. gr.	0·790

Recently Watermann and Heimel (40) investigated the effect of this hypochlorite treatment on hydrocarbon oil to which had been added small proportions of sulphur compounds. The following Table is the result of their work:-

TABLE IV.

Sulphur Compound	Sulphur % before treatment	Sulphur % after treatment
$(C_6H_5)_2S$	2·0	Practically free from sulphur
(C_6H_5) SH	1·70	0·4
$(C_2H_5)_2S$	1·80	0·5
(C_2H_5) SH	1·80	Practically free from sulphur
$C_6H_5N : C : S$	1·30	0·2
$C_6H_5S : CN$	1·30	0·5
CS_2	1·40	Practically free from sulphur
$(C_6H_5)_2SO_2$	0·30	" " " "
$(C_6H_5)_2SO$	1·30	0·4
$(C_2H_5)_2SO_2$	1·60	Practically free from sulphur
C_4H_4S	1·20	1·0
$C_2H_5S : CN$	1·60	Practically free from sulphur

These authors state that this process is suitable for desulphurising Mexican oils. In an example quoted, a Mexican oil containing 1·28% S had its sulphur content reduced by 68%.

PART II. (EXPERIMENTAL)

Isoamyl sulphide and its behaviour towards metallic chlorides, oxidising agents and materials which have the property of selectively adsorbing sulphur compounds.

Referring again to the work of Crooks on Scotch shale oil, it was noted that the unpleasant smell of this oil was due to sulphur compounds, and further, that these compounds were of the type that form compounds with mercuric chloride, viz: thioethers, disulphides, mercaptans, thiophenes or thiophanes. Mercaptans, however, would be removed to a great extent in the soda wash during refining. No positiv evidence of the presence of thiophene was obtained by the indophenine reaction. In view of this, and the fact that the endeavour to isolate the evil smelling sulphur compound from shale oil was unsuccessful, it was decided to prepare some thioethers and study their behaviour towards metallic chlorides, oxidising agents and materials such as bauxite and alumina.

Isoamyl sulphide (B.P. 212°C.), which falls within the distillation range of burning oil (150°C. - 275°C.), was first prepared by replacing the hydroxyl group of isoamyl alcohol with chlorine, and the subsequent interaction of the alkyl chloride and sodium sulphide. The formation of the chloride was attempted by two methods:-

(1) using phosphorous pentachloride

$$C_5H_{11}OH + PCl_5 = C_5H_{11}Cl + POCl_3 + HCl$$

(2) using phosphorous trichloride

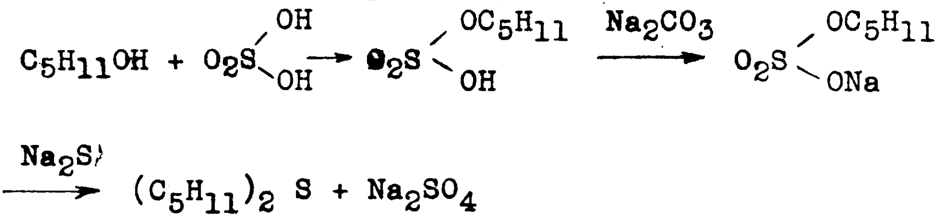
$$3\ C_5H_{11}OH + 2\ PCl_3 = 3\ C_5H_{11}Cl + P_2O_3 + 3\ HCl$$

The former method gave slightly better yield, but this was only 33% of the theoretical.

In the conversion of the chloride to the sulphide yields of only 30% calculated on the isoamyl chloride used were obtained, either in alcoholic or aqueous solution. This small yield was probably due to the formation of triamyl sulphonium chloride by the combination of isoamyl chloride and isoamyl sulphide.

$$(C_5H_{11})_2\ S + C_5H_{11}Cl \longrightarrow (C_5H_{11})_3\ S\ Cl$$

Thus the total yield of sulphide from alcohol was 12% of the theoretical yield. The method of preparation of the thioether finally adopted may be shown thus:-



$$C_5H_{11}OH + O_2S\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix} \longrightarrow O_2S\begin{matrix}\diagup OC_5H_{11}\\ \diagdown OH\end{matrix} \xrightarrow{Na_2CO_3} O_2S\begin{matrix}\diagup OC_5H_{11}\\ \diagdown ONa\end{matrix}$$

$$\xrightarrow{Na_2S} (C_5H_{11})_2\ S + Na_2SO_4$$

To 200 grammes of isoamyl alcohol were added gradually 400 grammes of concentrated sulphuric acid, the mixture being cooled after each successive addition. The product was then poured slowly into a litre of cold water, and the free acid neutralised with sodium carbonate solution, and a slight excess added. The whole was concentrated to about half its volume, allowed to cool, and the sodium sulphate removed. To the solution was added a solution of sodium sulphide, (prepared by saturating a 20% solution of caustic soda with hydrogen sulphide, and adding the necessary amount of caustic soda) and the mixture heated under a reflux condenser for one hour. The oily layer which separated out was removed, washed with caustic soda solution, dried and distilled. The portion boiling between 212°C. and 215°C. was retained as isoamyl sulphide. Later it was found that the yield of thioether was almost doubled if, instead of neutralising the sulphuric acid with sodium carbonate, milk of lime was used. The calcium sulphate was then removed, the calcium alkyl hydrogen sulphate converted to the sodium salt, and the calcium carbonate formed filtered off. As before, the solution was concentrated and treated with sodium sulphide. 120 grammes of isoamyl sulphide were prepared in this manner.

Action of Metallic Chlorides on Isoamyl Sulphide.

As is well known the alkyl sulphides form white, solid crystalline addition compounds with mercuric chloride, but they are also capable of forming additive compounds with a few other metallic chlorides. The following have been described:-

$Pd\,Cl_2\ 2(CH_3)_2S$, $CuCl\ (CH_3)_2S$, $AuCl(CH_3)_2S$

The possibility of the more common chlorides acting similarly was entertained and investigated.

To an alcoholic solution of the chloride was added a few cc. of isoamyl sulphide. The mixture was shaken for 30 minutes and allowed to stand for a few hours, when the effect on the unpleasant smell of the sulphide was noted. The results are shown below:-

	Chloride	Smell
1.	Mercuric chloride.......	destroyed
2.	Ferric Chloride.........	"
3.	Stannic chloride........	faint
4.	Stannous chloride.......	"
5.	Cupric chloride.........	very faint

No addition compound was thrown out, except the product of reaction with mercuric chloride. All chlorides partially destroyed the unpleasant odour of the thioether, while with the product of 1 and 2 this smell was completely absent.

The additive compound with mercuric chloride was of a white, crystalline nature, sparingly soluble in alcohol and ether. After being recrystallised four times from alcohol, the addition compound melted with decomposition at 114°C. Analysis showed this compound to have the formula $(C_5H_{11})_2S\cdot 2\ HgCl_2$. (Found 4·64% S required 4·46% S).

By heating the mercuric chloride addition compound to over 195°C. a volatile liquid containing chloride was obtained, while the residue consisted of mercury chloride and sulphide. It appears, therefore, that the compound $(C_5H_{11})_2S\cdot 2\ HgCl_2$ on being heated first decomposes at 114°C. into the thioether and mercuric chloride, and on still further heating, above 195°C., this mixture undergoes double decomposition to form isoamyl chloride and mercury sulphide, thus:-

$$(C_5H_{11})_2S\cdot 2\ HgCl_2 = (C_5H_{11})_2S + 2\ HgCl_2$$

$$(C_5H_{11})_2S + HgCl_2 = 2\ C_5H_{11}Cl + HgS$$

Hydrogen sulphide and caustic soda decompose this addition compound regenerating the thioether. As a means of extracting thioethers from burning oil, treatment with mercuric chloride followed by decomposition of the addition compound formed gave good results.

In one experiment 12 grammes of isoamyl sulphide were dissolved in one gallon of burning oil, and the mixture agitated for one hour with 70 grammes powdered mercuric chloride partially dissolved in alcohol. The addition compound was filtered off, drained and washed once with a small quantity of petroleum ether to remove any hydrocarbon oil. The residue was transferred to a flask, an excess of 30% caustic soda added, and steam distilled. The oily layer was separated, dried and distilled, when 8·2 grammes of isoamyl sulphide, or 68% of that added, were recovered.

Of the remaining chlorides, only ferric chloride appeared to be of service in destroying the smell of the sulphide, but any addition compound, if formed, was not thrown out of solution, even on the addition of water. Further experiments, carried out with the object of isolating an addition compound of isoamyl sulphide and ferric chloride, met with no success. It was established that this compound, if it existed, was decomposed under 142°C., that it was soluble in alcohol, and was not thrown out of solution on diluting the alcoholic solution with water.

Burning oil was treated with ferric chloride solution, but the product was very unsatisfactory. Particulars of the treatment were as follows:-

100 cc. of the oil were agitated for one hour with 50 cc. of a 10% aqueous solution of ferric chloride, washed with water, caustic soda solution, and again with water. The smell of the treated oil was only slightly improved, while the ferric chloride imparted a slight yellow colour

to the oil which, even on distillation, was not destroyed. The sulphur content of the oil was little reduced.

Sulphur content of burning oil before treatment = 0·148%
" " " " " after " = 0·145%
" " " " " " "
and distillation = 0·137%

Oxidation of Isoamyl Sulphide.

The bahaviour of isoamyl sulphide when treated with aqueous solutions of the oxidising agents, hydroegn peroxide chromic acid, acid potassium dichromate, and sodium hypochlorite, was now studied. Details of the experiments are given below:-

1. Hydrogen peroxide.

To five grammes of the sulphide was added an excess of a 30% solution of hydrogen peroxide, and the mixture allowed to stand for 48 hours. A crystalline body separated out which, when crystallised from petroleum ether, had a melting point of 34°C. (isoamyl sulphoxide melting point 35°C. Gadzer and Smiles (41). In a further experiment where ten grammes of the sulphide were treated, the product of oxidation was extracted with ether, dried, and the ether removed. The residue, on distillation, began to decompose about 220°C. into evil smelling products. The distillation was continued under reduced pressure, 76 mm. Hg., when the whole distilled over between 175 and 180°C. The distillate was solid at room temperature, and on being crystallised from petroleum ether, cooled in a freezing mixture, had a melting point of 34°C. On analysis this product gave 16·79% S - $(C_5H_{11})_2SO$ requires 16·85% S.

(Note:-The boiling point of isoamyl sulphide at 76 mm.Hg. pressure is 142°C.

2. Chromic acid.

To a solution of the thioether in glacial acetic acid was added a solution of chromic acid in the same solvent. After standing for half-an-hour the product was diluted, and the acid neutralised with caustic soda. The alkaline solution was extracted with ether, the ethereal solution dried, and the ether removed. The residue was a white solid which, on crystallising from petroleum ether, had a melting point of 34°C. - again the sulphoxide.

3. Potassium dichromate.

Ten grammes of isoamyl sulphide were heated under a reflux condenser with an excess of 8% acid potassium dichromate solution for one hour. As before, the product was extracted with ether and dried. After distilling off the ether the residue was fractionally distilled under reduced pressure - 76 mm. Hg. - 1·7 grammes of unchanged isoamyl sulphide were recovered, while all except 2 grammes distilled over between 175-180°C. The residue was of higher boiling point. Thus 80% of the alkyl sulphide was oxidised, 60% to the sulphoxide, while the remainder probably had been further oxidised to the sulphone.

In a similar experiment where the sulphide was treated with the oxidising agent, in the cold, 60% of the thioether was attacked.

4. Sodium hypochlorite.

Thirteen grammes of isoamyl sulphide were agitated for one hour with an excess of sodium hypochlorite solution (prepared by passing chlorine into a 25% solution of caustic soda, kept cool by immersion in an ice bath). The products of this treatment were extracted with ether, dried, and the ether distilled off. The residual liquid was fractionally distilled three times, when ultimately about one gramme of a liquid boiling between 175°C. and 180°C. at 76 mm. Hg. pressure was collected, i.e. one gramme of isoamylsulphoxide.

Isoamyl sulphide was now subjected to a similar treatment with a more active solution of hypochlorite, viz: of strength 0·3 N containing 0·7 grammes of free caustic soda per litre. Fifteen grammes of sulphide so treated yielded 10 grammes of a liquid of boiling point 191°C. under a pressure of 18 mm. This, on cooling, solidified, and after crystallisation from petroleum ether, cooled in a freezing mixture, melted at 25-26°C. (isoamylsulphone melting point 31°C. Gadzer and Smiles (41). On analysis it was found to contain 16·31% S.-$(C_5H_{11})_2SO$ requires 16·85% S and $(C_5H_{11})_2SO_2$

requires 15·53% S.) The product of this treatment is therefore a mixture of the sulphoxide and sulphone. On distilling this product at atmospheric pressure it distilled at 295-296°C., but at the same time it partly decomposed, with the result that the distillate had a particularly bad smell.

Conclusions.

Isoamyl sulphide was oxidised in the cold by dilute solutions of oxidising agents to either the corresponding sulphoxide or sulphone.

Both these compounds are neutral bodies and cannot be removed by a soda wash.

On distillation at atmospheric pressure the sulphoxide begins to decompose about 220°C.

Sodium hypochlorite solution of strength 0·2N to 0·3N containing 0·5 to 1 gramme of free caustic soda per litre proved to be the most active oxidising agent tried. Isoamyl sulphide treated with such a solution was oxidised to a mixture of isoamylsulphoxide and isoamylsulphone. This product, on distillation at atmospheric pressure, was partly decomposed, yielding an evil smelling distillate.

Action of Bauxite and Floridin on Isoamyl Sulphide.

It is well known in the petroleum industry that bauxite and floridin and certain dehydrated clays possess the property of selectively adsorbing sulphur compounds from hydrocarbon oils. A few experiments have been completed with the object of ascertaining the behaviour of isoamyl sulphide when brought into contact with such materials. The method of carrying out the experiments was to add to a sweet smelling oil (White Rose Paraffin - S. 0·095%) a quantity of the alkyl sulphide (which increased the sulphur content of the oil to 0·23%) and filter the mixture through a column of material under examination. Bauxite and floridin were tried. Both were ignited at 700°C., cooled in a dessicator, and packed in a tube 24" long and of diam. ½". The oil was allowed to filter through this column of material (18" in length) and collected in fractions of 25 cc. The following table shows the effect on the sulphur content of the oil:-

TABLE V.

		Sulphur %				
Matl.	Wt. gms.	1st Fract. 0-25cc.	2nd Fract. 25-75cc.	3rd Fract. 75-125cc.	4th Fract. 125-175cc.	Last Fract. cc.
Bauxite	57	0·099	0·181	0·215	0·224	3·5
Floridin	47	0·188	0·210	0·215	0·224	3·5

Oil recovered by washing spent bauxite with water = 12 cc.
" " " " " floridin " " = 11 cc.

Sulphur in original oil = 0·23%

From the above it is seen that while there is a distinct adsorption of isoamyl sulphide especially noted in the first 75 cc., the quantity of material required to completely remove the sulphide is too great to be of value in deodorising oil. The smell of the first 75 cc. was very good, but in the remaining portions the odour of isoamyl sulphide was evident.

Preparation and Oxidation of the Unsaturated Hydrocarbons, Isoamylene, Di-isoamylene and Tri-isoamylene.

The foregoing experiments on the oxidation of isoamyl sulphide having shown the product of oxidation, the sulphoxide and sulphone, to be sweet smelling compounds, it was felt that by treating 'Scotch' burning oil with an oxidising agent, the desired deodorisation might be attained. In considering the possible employment of oxidising agents, the effect of these on saturated and unsaturated hydrocarbons must be borne in mind, especially the latter, which is present in shale oil to the extent of about 40%. Below is given an account of the oxidation of isoamylene, di-isoamylene and tri-isoamylene.

Attempts were made to prepare isoamylene by dehydrating isoamyl alcohol with the following reagents, but with only moderate success:-

1. Aqueous zinc chloride.
2. Fused zinc chloride (42).
3. Concentrated sulphuric acid (43).

By these three methods only small quantities of isoamylene were obtained. ADAMS, KAMM & MARVEL ~~Senderens~~ (44), however, obtained a 80% yield of isoamylene by passing isoamyl alcohol over alumina heated at 540°C. Using bauxite in place of alumina, the author of this Thesis found that at 540°C. isoamylalcohol was completely decomposed into gaseous products. On dropping the temperature of the bauxite to

350°C. the dehydration of the alcohol proceeded smoothly; 70% of the alcohol was attacked in one passage over the bauxite. Unchanged isoamylalcohol was subsequently converted into isoamylene by a further treatment. The products of decomposition of the alcohol were isoamylene and water. The water was separated and the isoamylene distilled off, leaving a small residue of unchanged isoamyl alcohol. The distillate was dried over calcium chloride and redistilled, using an eight bulb Hempel fractionating column, the portion boiling between 31 and 36°C. being collected. This apparently contained a mixture of α, β, γ γ isoamylenes (boiling points - 36°C., 31°C. and 32°C. respectively).

Di-isoamylene and tri-isoamylene were prepared by polymerisation of this olefine. As polymerising agents, both zinc chloride and ignited floridin (45) failed, but anhydrous aluminium chloride (46) was so violent that the product was a dark coloured heavy oil. The action was considerably modified by adding the chloride to a solution of the olefine in ether, the extent of the reaction depending on the volume of ether used. The mixture which yielded the greatest quantities of di-isoamylene and tri-isoamylene was 2 parts by volume of isoamylene to 1 part by volume of ether. The method of preparation was to add gradually the anhydrous chloride to the ethereal solution of the olefine and allow the mixture to stand overnight. The mixture was poured into water, the water separated, and the ethereal solution washed with caustic soda solution, and dried over anhydrous sodium sulphate. From this dry product the unchanged isoamylene and ether were removed by fractional distillation, and the residue carefully fractionated into four portions. In one experiment 100 cc. of isoamylene yielded the following fractions:-

(1) 60°C. - 150°C. ......16 cc.
(2) 150°C. - 165°C. ......25 cc.
(3) 175°C. - 240°C. ...... 6 cc.
(4) 240°C. - 270°C. ......11 cc.

Molecular weight determinations (freezing point method) of fractions (2) and (4) showed them to be di-isoamylene (molecular weight found 144 - theoretical 140), and tri-isoamylene (molecular weight found 218 - theoretical 210) respectively. Later it was established that by adding small quantities of concentrated sulphuric acid to isoamylene, polymerisation took place, and that by adjusting the quantity of acid used it was possible to regulate the action so that di- or tri-isoamylene may preponderate as desired.

Oxidation of isoamylene, di-isoamylene and tri-isoamylene.

An exhaustive examination of the products of the oxidation of isoamylene has been carried out by Zeidler (47) The oxidation, however, was carried out in sealed tubes, if necessary at 90°C., heating being continued in some cases for several days. For the present purpose, oxidation at room temperature, during one hour, was all that was necessary. Thus, while the method of treating the olefines consisted of agitation with the oxidising agent at room temperature for one hour, the examination of the products was essentially that of Zeidler. The product of this treatment was acidified with dilute sulphuric acid and steam distilled, thereby removing the volatile acids and leaving the fixed acids in the residue (R_1). The distillate was made alkaline with caustic soda, and the unchanged isoamylene removed by distillation. This residue (R_2) was acidified and again steam distilled, and the distillate examined for volatile acids. The non-volatile acids (R_1) were neutralised with caustic soda and evaporated to dryness, and the residue taken up with absolute alcohol. The alcoholic solution was saturated with carbon dioxide, and again brought to dryness. This residue was again taken up with absolute alcohol, and after filtration, was tested for succinic acid. The residue from the first alcoholic extraction was examined for oxalic acid. In no case were the products of oxidation present in sufficient quantity to isolate any derivative or salt of them, their presence or absence being ascertained by wet way reactions.

By this method isoamylene was found to yield with:-

1. 10% hydrogen peroxide solution - small quantities of formic and acetic acids with traces of oxalic and succinic acids.

2. 10% acid potassium dichromate solution - small quantities of acetic, oxalic and succinic acids.

The extent of the oxidation of isoamylene, di-isoamylene and tri-isoamylene, or rather the loss of these hydrocarbons, when treated in the cold with the two oxidising agents, was determined as described below:-

A glass vessel consisting of two bulbs of 200 cc. capacity connected by a graduated tube 10 cms. in length, the lower bulb being fitted with a stop-cock, while the other was closed by a ground glass stopper, was filled up to the zero mark with the oxidising agent. About 10 cc. o the unsaturated hydrocarbon were run in, and its volume measured in the graduated portion. The vessel was then agitated in a mechanical shaker for one hour, the contents allowed to separate, and the oxidising agent run off. To the residue was added 200 cc. of dilute caustic soda solution, and the whole again agitated. On settling,the volume of unchanged hydrocarbon was noted, the diminution in volume being taken as the amount oxidised, subject to a slight correction for the solubility of the unsaturated hydrocarbon in water and caustic soda solution. This correction was determined by blank estimations.

The volatile acids formed were estimated by steam distilling the acid solution of the oxidising agent, plus the acidified solution from the caustic soda wash. The results are noted in Table VI. The volatile acids are given as the equivalent in grammes of acetic acid per 100 cc. of hydrocarbon.

TABLE VI.

	% of Hydrocarbon oxidised		Volatile acids	
	H_2O_2	$K_2Cr_2O_7$	H_2O_2	$K_2Cr_2O_7$
Isoamylene	0·7	13·4	0·39	5·4
Di-isoamylene	0·8	3·0	0·40	0·45
Tri-isoamylene	1·0	7·0	-	-

A survey of these few experiments with isoamyl sulphid show that this body is readily oxidised to the sweet smelling sulphoxide, and sulphone and that the unsaturated hydrocarbons examined, especially the higher members, di-isoamylene and tri-isoamylene, are much more slowly attacked by oxidising agents than the sulphide. This indicated the possibility of deodorising the oil by an oxidising treatment without fear of incurring any serious loss of hydrocarbons.

Oxidising Treatments of Burning Oil.

Burning oil was treated with (1) acid potassium dichromate solution, and (2) sodium hypochlorite solution with the results shown:-

(1) Treatment of burning oil with acid potassium dichromate.

100 cc. of the oil were shaken up with 10% solution of acid potassium dichromate, the dichromate run off, the residue washed with caustic soda 5% solution, and finally with water.

Distillation tests and iodine number determinations of the untreated and treated oils gave practically the same figures, while repeated tests for the presence of (OH) groups in the treated oil yielded negative results. (The acetyl value of the carefully dried oil was zero). Indeed, as far as could be seen, the character of the oil was unchanged.

The smell of the treated oil was much more pleasant, but the colour greatly inferior. On distillation, a sharp pungent odour was evident, while the colour was only slightly improved.

Below are the sulphur content and iodine numbers of the oils:-

	Sulphur %	Iodine No.
Original oil	0·148	74·5
Oil after potassium dichromate and soda treatment	0·139	75·0
Oil after above treatment and distillation	0·128	75·5

By substituting a filtration through bauxite for the final distillation, it was hoped to improve the colour of the product.

200 cc. of the oil were treated with -

1. 10% of a 10% acid solution of potassium dichromate,
2. washed with 10% of a 5% solution of caustic soda,
3. washed with water,
4. filtered through bauxite - weight 60 grammes, height of column 18", diam. ½".

The filtered oil was collected in four fractions, and the sulphur content of each determined as shown:-

	1st Fract.	2nd Fract.	3rd Fract.	4th Fract.
	0 - 25 cc.	25 - 75 cc.	75 - 125 cc.	125 - 175 cc.
Sulphur %	0·07	0·119	0·128	0·137

Mean sulphur content 0·120%.

The smell of the oil thus obtained was good, as was also its colour, which did not deteriorate on exposure to diffused light for two months.

About a gallon of burning oil was treated in this manner, but the bauxite was reduced to 2 lbs. per gallon, which gave an oil slightly inferior both in colour and smell.

(2) <u>Treatment of burning oil with hypochlorites.</u>

The method of refining petroleum distillates by dilute hypochlorite solutions (A.E. Dunstan) (33) which has been successful in removing the sulphur, and incidentally the offensive odour from various petroleum oils, particularly Persian oil, has been applied to 'Scotch' burning oil with the results detailed below.

The burning oil was subjected to the treatment outlined by Dr. Dunstan in the paper referred to, viz:

1. An initial soda wash.
2. A water wash.
3. First hypochlorite treatment.
4. Second hypochlorite treatment.
5. Final soda treatment.
6. Water wash.
7. Filtration through bauxite (a) 2 lbs. bauxite per gallon of oil, (b) 4 lbs. per gallon.

Particulars of each stage were as under. The agitation in all cases was accomplished by a mechanical shaker.

1. The oil was agitated for half-an-hour with 3% of a 10% caustic soda solution, allowed to settle for about 10 minutes, and the soda solution run off.

3. After washing with water, the oil was agitated with 20% by volume of a 0·3N sodium hypochlorite solution for 30 minutes, allowed to settle for 15 minutes and the spent solution removed.

4. This was carried out exactly as in 3.

5. The strength of the soda solution and duration of the wash were as in treatment No. 1.

7. The bauxite was activated by heating to 550°C., cooled in a dessicator, and charged into a perpendicular glass tube. The height of the column of bauxite was 18", its

diameter $\frac{1}{2}$", and the weight of bauxite used was 68·4 grammes. The oil, after the final soda and water wash, was divided into two portions, the first being filtered through the material in the proportion of 2 lbs. per gallon, the second 4 lbs. per gallon.

The hypochlorite solution was prepared by passing chlorine into a 10% caustic soda solution, until the strength reached about 2N available chlorine, with 5-6 gms. of free caustic soda per litre. This, diluted with 6 volumes of water gave a solution about 0·3N containing 0·5 to 1·0 gm. of caustic soda per litre. The available chlorine and free caustic soda were determined by taking 5 cc. of the solution, adding an excess of standard hydrochloric acid, and then potassium iodide solution. The iodine liberated was titrated with sodium thiosulphate solution. Methyl orange was now added, and the excess of hydrochloric acid estimated with standard sodium carbonate solution.

Two samples of 'Scotch' burning oil (A. and B.) were treated in the above manner. The following Table shows the amount of sulphur removed at each stage:-

TABLE VII.

	A.		B.	
	Sulphur %	% of total sulphur removed	Sulphur %	% of total sulphur removed
Untreated oil	0·127	-	0·127	-
Oil after initial soda treatment	0·123	3·1	0·121	4·7
Oil after 1st hypochlorite treatment	0·115	6·3	0·115	4·7
Oil after 2nd hypochlorite treatment	0·110	4·0	0·117	nil
Oil after final soda and water wash	0·112	nil	0·113	1·6
Oil after filtration through bauxite -				
* 2 lbs. per gal.	0·107	2·4	0·110	2·4
4 " " "	-	-	0·098	9·4
Total sulphur removed		15·8		22·8
Total sulphur removed excluding bauxite treatment		11·8		11·0

* Chlorine content = 0·02%
* Iodine No. = 83·3
Untreated oil " " = 84

The strength of the hypochlorite solutions before and after the treatments were as under:-

TABLE VIII.

	A.		B.	
	Strength of hypochlorite solution	Free alkali gms/litre	Strength of hypochlorite solution	Free alkali gms/lit.
Before treatment	0·303 N.	0·74	0·292 N.	0·80
After 1st treatment	0·112 N.	-	0·074 N.	-
" 2nd "	0·193 N.	-	0·216 N.	-

The treated oil, after the final soda wash, had lost entirely its characteristic smell, but had a peculiar faint odour, not unpleasant, similar to that of an oil treated with potassium dichromate. The colour of the oil at this stage was deeper than that of the original sample. Very little sulphur, however, had been removed. A distillation of the oil resulted in the generation of a sharp unpleasant odour similar to that obtained on distilling a dichromate treated oil. Here again, the conclusion is drawn that an oxidising treatment oxidises the evil smelling sulphur bodies to sweet smelling compounds, which are not removed by caustic soda solutions and which, on distillation, break down into unpleasant smelling products.

The lighter bauxite treatment, 2 lbs./gal.,removes another 4 to 5% of sulphur, and improves the colour of the oil slightly. The heavier treatment, 4 lbs./gal., besides giving an almost water-white oil, reduces its sulphur content by about 11%. The smell of this product is very good.

Conclusions.

As the loss of oil in these oxidising treatments is small, and the resultant product has a greatly improved odour, these processes appear to deserve careful consideration. It must be remembered, however, that while the smell of the oil is much more pleasant, the sulphur is not removed - merely oxidised - and should the treated oil be distilled an unpleasant smell is generated.

PART III. (EXPERIMENTAL)

THE CATALYTIC DECOMPOSITION OF THE UNPLEASANT SMELLING SULPHUR COMPOUNDS OF 'SCOTCH' BURNING OIL.

Hydrogenation of Burning Oil.

A. Catalyst - nickel.

Although in Parts I and II the unpleasant smell of the oil was proved to be due mainly, if not entirely, to sulphur compounds, there still remained the possibility of unsaturated hydrocarbons being partly responsible. The unsaturated hydrocarbon content of Scotch burning oil is of the order of 40%, and therein lies the main difference between it and the corresponding refined oil from American petroleums, the latter being practically free from unsaturated hydrocarbons. With the object of preparing from 'Scotch' burning oil a product similar to this American burning oil, a few experiments were undertaken on the hydrogenation of this oil.

The hydrogenation of the unsaturated constituents of mineral oil has proved to be a fascinating study to chemists, and the literature on the subject is voluminous. Most of the work, however, deals with the cracking of heavy oils,and the subsequent hydrogenation of the products formed; on the hydrogenation of shale oil little is to be found. Crooks (48) attempted to hydrogenate 'Scotch' burning oil in the liquid phase, using a nickel catalyst at 170°C. under atmospheric pressure, but met with only slight success. Oil of iodine No. 75, after six hours' treatment with hydrogen, only absorbed sufficient hydrogen to lower the iodine No. to 66·6. Further experiments by this author led to similar results.

Assuming this to be due to the poisoning of the catalyst by the sulphur in the oil, the hydrogenation was now attempted, using a nickel oxide catalyst, which is stated to be less sensitive to sulphur bodies (49). This catalyst was prepared according to the method of Bedford and Erdmann (50) in which a solution of nickel nitrate and sugar is dropped on to a surface at low red heat. The product so prepared is very light and contains - carbon 0·42%, hydrogen 0·66% and nickel 76·67%. The calculated quantity of nickel in nickel oxide is 78·57%. A feature of this catalyst is that, being so bulky, it is very easily distributed throughout the oil. To still further reduce the possibility of sulphur poisoning the catalyst, this element was partially removed from the oil by an exhaustive filtration through bauxite. Thus the sulphur content of the oil was reduced from 0·15% to 0·07%.

The experiment was carried out as follows:- A litre round bottomed flask, fitted with a large reflux condenser and an inlet tube for hydrogen, was charged with 300 cc. of this partially desulphurised burning oil and three grammes of nickel oxide catalyst. This mixture was maintained at a temperature of 180°C., while pure dry hydrogen bubbled through it. After three hours' treatment no fall in the iodine No. of the oil was found. Further attempts on these lines yielding no better results, the hydrogenation of oil in the liquid phase was discontinued.

Attention was now directed to the hydrogenation of the oil by passing it as vapour, mixed with hydrogen, over finely divided nickel, deposited on an inert material such as pumice at 300°C. This met with moderate success.

To prepare the catalyst a quantity of nickel nitrate was dissolved in water, the solution concentrated, and granulated pumice stone added (size of pumice - such that it passed through $\frac{1}{4}$" sieve and was retained on $\frac{1}{8}$" sieve). After standing thus for a short time, the nickel hydroxide was precipitated on to the pumice stone with a slight excess of caustic soda solution. This mixture was now filtered off, washed until free from alkali, and dried. This dry material was packed into a combustion tube (diam. $\frac{1}{2}$" and length 3') having a side tube at one end to permit of the withdrawal of the products of the reaction, and the introduction of a thermocouple. The whole was then surrounded with asbestos, and placed in a gas-fired furnace. The temperature was measured by a nickel-nichrome thermocouple embedded in the centre of the reaction tube. The hydroxide was then reduced to the metal at 300°C. with pure dry hydrogen. When the reduction was complete, 100 cc. of the oil, partially desulphurised by a preliminary bauxite treatment, were vaporised, mixed with hydrogen and passed through the reaction tube, which was still maintained at a temperature of 300-320°C. The liquid product was condensed and collected in a receiver, while the excess hydrogen was led off and burned. The rate of flow of hydrogen was measured by passing the gas through a fine jet, the difference in pressure of the gas on either side of the orifice indicating the rate of flow.

Particulars of the experiment are as shown below:-

Weight of nickel = 13 grammes - 63 grammes $Ni(NO_3)_2 6H_2O$
" " pumice = 39 "
Temperature of reduction of nickel = 300°C.
" " hydrogenation of oil= 300-320°C.
Volume of oil treated = 100 cc.
Rate of flow of oil = 100 cc./90 min.
" " " " hydrogen = 10 litres/hour.

	Sulphur %	Iodine No.
Oil before hydrogenation	0·086	73·1
" after "	0·007	21·0

The product of this treatment was a water-white oil free from the characteristic smell of Scotch burning oil.

The sulphur content was reduced to a negligible quantity and, while the oil was not completely hydrogenated, only one-third of the unsaturated bodies remained unchanged. By repeatedly passing the oil vapour with hydrogen as above, it was found possible to reduce the unsaturated hydrocarbons to a very small proportion (iodine No. 3·7), and to eliminate the sulphur entirely. This final product of repeated hydrogenation differs, if at all, only slightly from the very best petroleum products. It retains no trace of the unpleasant odour of shale oil, and is water-white even now after standing in diffused light for two years.

Below are given details of this last experiment:-

Volume of oil treated = 490 cc.

	Sulphur %	Iodine No.
Oil after 1st passage over catalyst	0·007	28·0
" " 2nd " " "	trace	11·1
" " 3rd " " "	-	5·8
" " 4th " " "	-	3·7
Untreated oil	0·086	72·5

The success of the above experiments indicated that such a treatment would probably deodorise, partially desulphurise, and partially hydrogenate burning oil which had not been subjected to a preliminary bauxite treatment. This was demonstrated in the following series of experiments which had as an additional object the investigation of the rate of deterioration of the catalyst. Here 1000 cc. of burning oil (S = 0·148%) were vaporised and passed with hydrogen over nickelised pumice at 300°C.; this operation was carried out in ten lots of 100 cc. each. The sulphur content and iodine No. of each portion were determined, giving the figures shown in Table IX:-

TABLE IX.

Distillate	Sulphur %	Iodine No.
1st 100 cc.	0·028	41·5
2nd "	-	28·9
3rd "	0·035	32·1
4th "	-	33·6
5th "	0·059	36·8
6th "	-	39·8
7th "	0·157	45·6
8th "	-	43·1
9th "	0·072	55·2
10th "	0·077	52·3
Mean value for 1000 cc.	0·055	41·0
Untreated oil..	0·148	75·0

Table IX shows a gradual decrease in the activity of the catalyst corresponding with a decrease in the amount of sulphur removed from the oil, and the hydrogen added. Nevertheless, the product in all cases bore no trace of the unpleasant odour of shale oil. The colour of the treated oil especially of the first 500 cc., while not quite water-white, was nearly so, and altered but little on exposure to diffused light for three months. Towards the end of the experiment the colour was not quite so good, but was still much better than that of the original oil. While about

50% of the unsaturated hydrocarbons were attacked, tests on the "distillation range" and specific gravity of the products showed no variation from those of a normal burning oil.

Throughout the experiment the excess hydrogen was passed through a trap containing lead acetate, but no hydrogen sulphide was detected in the escaping gas. All the sulphur taken from the oil combined with the nickel, a fact verified by an examination of the spent catalyst.

B. Catalyst - copper.

Copper and iron were now considered as substitutes for nickel. Metallic copper was deposited on pumice stone in the same manner as described for nickel, except that, since copper oxide was found to be less easily reduced, a temperature of 400°C. was employed in the reduction. The modus operandi was exactly as described in the last experiment with nickel as catalyst. 700 cc. of oil were treated and collected in 100 cc. portions. Table X shows the result:-

TABLE X.

Distillate	Sulphur %	Iodine No.
1st 100 cc.	0·095	68·3
2nd "	-	72·1
3rd "	0·133	72·3
4th "	-	73·7
5th "	0·136	74·3
6th "	-	73·5
Untreated oil...	0·148	75·0

Copper was not nearly so active as nickel, either as a catalyst for the decomposition of the sulphur compounds, or for hydrogenating the oil. A trace of the original smell still remained in the oil, and further, the treatment imparted a faint yellow colour to the oil which increased as the experiment proceeded.

The experiment was repeated at a higher temperature. 100 cc. of oil were vaporised and mixed with hydrogen,and passed over finely divided copper at 400°C. The sulphur content of the oil obtained under these conditions was 0·118%, while the colour was more intense.

In both experiments the sulphur removed from the oil united with the metallic copper.

C. Catalyst - iron.

After the manner described in A and B, the activity of iron as a catalyst in the hydrogenation and desulphurisation of Scotch burning oil was determined. The method of preparation of the metal was slightly different, viz: 280 grammes of iron nitrate,($Fe(NO_3)_3 9H_2O$), equivalent to 37 grammes of iron was dissolved in water, boiled, filtered and concentrated. To this was added 150 grammes of granular pumice and, after standing, an excess of ammonium hydroxide. This mixture of hydroxide and pumice was filtered off, washed and heated to drive off the last traces of ammonia. The

The oxide was then reduced with pure dry hydrogen at 400°C.

The remainder of the process was exactly as in A and B. 700 cc. of oil were treated and collected in portions of 100 cc. The iodine number and sulphur content of the various portions were determined, and the results are shown in Table XI:-

TABLE XI.

Distillate	Sulphur %	Iodine No.
1st 100 cc.	0·091	64·1
2nd "	-	68·7
3rd "	0·135	70·8
4th "	-	72·8
5th "	0·137	72·0
6th "	-	71·3
7th "	0·140	70·9
Mean value for 700 cc.	0·126	70·1
Untreated oil...	0·148	74·5

As a catalyst in deodorising and desulphurising burning oil, iron ranks with copper, but in hydrogenating the oil, iron had a slight advantage over the latter. The colour of the product, however, was much better than in the case of copper, the first 200 cc. being practically water-white, but on standing exposed to light for three weeks a distinct yellow tinge developed.

Conclusions.

In hydrogenating burning oil the best results were obtained with the oil in the vapour phase, and with finely divided nickel as catalyst. In this respect, copper and iron were inferior to nickel. If the oil be previously partially desulphurised by bauxite treatment, it can be almost completely hydrogenated. During hydrogenation the oil was deodorised and partially desulphurised. This is in accordance with the work of Evans (51), who made this fact the subject of a patent. The activity of the catalysts decreased as the sulphur was extracted from the oil, i.e. as the catalysts became gradually converted to the various sulphides. As will be demonstrated later, the lower sulphides do act catalytically in decomposing certain sulphur compounds.

Partial Deodorisation and Desulphurisation of Burning Oil by passing the Oil Vapour over finely divided Metals and Metallic Oxides.

By simply bringing the oil vapour into contact with finely divided metals at 300°C.-320°C. it now seemed likely that the desired deodorisation of the oil would be attained. This point was investigated by passing the oil as vapour, without hydrogen, through a tube containing the metals - nickel, copper and iron, in exactly the same manner as in the hydrogenation experiments.

A. Nickel.

300 cc. of burning oil were treated and collected in portions of 100 cc. The result, however, was disappointing The product, while much improved in smell, had a distinct green colour, which was retained even when the oil was redistilled. The sulphur content of the oil was slightly reduced, but not to anything like the same extent as when hydrogen was mixed with the oil vapour. The sulphur content and iodine number of the various portions are given:-

TABLE XII.

Distillate	Sulphur %	Iodine No.
1st 100 cc.	0·077	70·7
2nd "	0·091	71·8
3rd "	0·096	74·6
Untreated oil....	0·148	74·5

Repeated passage of the oil vapour over the finely divided nickel led to only a slight increase in the amount of sulphur removed, while the colour of the treated oil became more pronounced as the experiment progressed.

250 cc. of burning oil passed repeatedly over the heated catalyst as described, gave the following results:-

Sulphur content of oil after passing once over the catalyst.......................... = 0·083%
Sulphur content of oil after passing three times over the catalyst............... = 0·079%
Sulphur content of oil after passing five times over the catalyst............... = 0·072%

B. Copper.

With copper a similar experiment yielded worse results. The depth of colour of the treated oil was greater than the corresponding experiment in which hydrogen was used. The unpleasant smell of the untreated oil was not destroyed, only slightly improved.

500 cc. of oil were treated and collected in portions of 100 cc. The sulphur content of the products are shown below:-

	Sulphur %
1st 100 cc.	0·129
2nd "	0·132
3rd "	0·136
Untreated oil..	0·148

C. Iron.

The effect of passing the oil vapour over finely divided iron at 300°C. as in the case of copper and nickel was not encouraging. Again, the smell of the treated oil, while not destroyed completely, was improved. The product was slightly coloured, but not to the same extent as with nickel and copper. This colour was proved by analysis to be due to a small quantity of dissolved iron.

500 cc. of oil were treated and collected in portions of 100 cc.

TABLE XIII.

	Sulphur %
1st 100 cc.	0·117
3rd "	0·134
5th "	0·134
Untreated oil...	0·148

D. Ferric oxide.

Two experiments were carried out, one at 300°C. and one at 400°C, on the distillation of burning oil over pumice carrying finely divided ferric oxide. The oxide was prepared in the same manner as the metallic iron in the previous experiments, omitting, of course, the reduction process. The sulphur content of the oil after distillation over the oxide at the temperatures mentioned was as follows:

1. At 300°C. - 0·109% S.
2. At 400°C. - 0·113% S.

The amount of sulphur removed at 300°C. was of the same order as when metallic iron was used, whilst at 400°C. no further quantity of sulphur was eliminated. The colour of the oil was much darker in the corresponding iron experiment and that got at 400°C. was still more intense.

Conclusions.

In contrasting the products obtained in this series of experiments with the corresponding experiments on the hydrogenation of the oil, it was obvious that the presence of hydrogen resulted in a very marked increase in the amount of sulphur eliminated from the oil. While the smell of the oil in the former case was improved, the product of the hydrogenation experiments was practically free from the characteristic smell of Scotch oil. The colour of the treated oils was also noteworthy. Those obtained in the series not using hydrogen were distinctly coloured. With nickel, the colour was of a greenish tinge, with copper, rather more yellow, and with iron, again green. A number of experiments were carried out on this subject, but only in the case of iron did tests for the metals yield positive results.

Decomposition of Isoamyl Sulphide and Thiophene.

At this stage, a study of the behaviour of thioethers and ring sulphur compounds when vaporised, mixed with hydrogen, and brought into contact with finely divided metals, was decided upon. Isoamyl sulphide was taken as representing the alkyl sulphides, while the ring sulphur compound chosen was thiophene.

Isoamyl sulphide.

This sulphide was distilled, its vapour mixed with hydrogen, and passed through a reaction tube containing finely divided nickel deposited on pumice stone, maintained at 300°C. The contact material was prepared, and the experiment carried out in a similar manner to the experiments on the hydrogenation of burning oil. In this case, however, a longer reaction tube was required to permit of the use of sufficient nickel to satisfy all the sulphur in the isoamyl sulphide, and, in addition, have a slight excess. The products of the interaction were cooled in an air condenser, a double surface water condenser, and then passed to a receiver immersed in a freezing mixture at -10°C. Here the liquid products were retained while the gaseous products were led into an aspirator fitted with a device for collecting a gas under constant pressure. Details of the experiment are as under:-

Isoamyl sulphide treated = 30 cc.
" " recovered = 12·5 cc.
Nickel used = 30 grammes
Pumice used = 120 grammes
Rate of flow of hydrogen = 10 litres/hour
Rate of distillation of sulphide= 10 cc./hour

The liquid product, on distillation, yielded a volatile liquid, 6·5 cc., and unchanged isoamyl sulphide. The volatile liquid was partly unsaturated,and distilled over between 26°C. and 31°C. When treated with bromine at -10°C. this liquid was only partly brominated. The portion unattacked proved to be a saturated hydrocarbon of boiling point 30°C. The liquid product of the above treatment was therefore isoamylene and isopentane. The gaseous product collected while the first 20 cc. of isoamyl sulphide were treated consisted of unsaturated and saturated hydrocarbons, together with the excess hydrogen, but only a trace of hydrogen sulphide. Towards the end of the experiment large volumes of hydrogen sulphide appeared with the excess hydrogen.

A similar experiment was carried out without hydrogen. Here the products obtained were unchanged isoamyl sulphide, 16 cc., and a small quantity, 7 cc., of an unsaturated liquid boiling between 27°C. and 30°C. This liquid had an iodine number of 259; on being treated with bromine at -10°C the low boiling liquid was all converted to a high boiling brom compound. It appears therefore that no saturated hydrocarbon was formed, and that the liquid product was isoamylene.

These results indicated that the thioether was decomposed with the formation of hydrogen sulphide according to either or both the equations:-

I. $(C_5H_{11})_2S + H_2 = 2\ C_5H_{12} + H_2S$

or II. $(C_5H_{11})_2S = 2\ C_5H_{10} + H_2S$

Certainly, in the second experiment, equation II represents the reaction. Thus the formation of pentane may be due entirely to subsequent hydrogenation of the olefine. The hydrogen sulphide combines with the nickel so that the complete interaction may be represented:-

$$(C_5H_{11})_2S = 2\ C_5H_{10} + H_2S$$

$$C_5H_{10} + H_2 = C_5H_{12}$$

$$H_2S + Ni = NiS + H_2$$

The presence of hydrogen increases the rate of decomposition of the thioether. This point is discussed later.

The efficiency of iron as a contact material in the decomposition of isoamyl sulphide at 300°C. was determined by exactly the same method as above. This, however, prove to be less satisfactory. When the sulphide was passed over the finely divided metal with hydrogen, only 39% of the sulphide was decomposed. When the sulphide alone was so treated only 20% was decomposed. In the former case, a small quantity of a volatile liquid partially unsaturated, of boiling point 26-30°C., was again obtained. The gaseous products, as with nickel, were saturated and unsaturated hydrocarbons, together with the excess hydrogen.

Assuming that the speedy removal of hydrogen sulphide would promote the decomposition of the thioether, a strong basic substance - lime - was tried in place of the metallic catalyst. This, however, yielded worse results. The iso-amyl sulphide was brought into contact with lime, both in the presence of hydrogen and alone, but the amount of sulphide decomposed was of the order of 5% in each case.

Thiophene.

In a similar manner to that detailed above, thiophene was vaporised, mixed with hydrogen, and passed over finely divided nickel. An additional receiver, cooled in liquid air, was added to the apparatus. At 300°C. the decomposition was barely perceptible; the only indication of its having taken place at all was the presence of a small quantity of nickel sulphide in the catalyst.

At 500°C., however, the action was appreciably greater, but was still very slow. Here 87% of the thiophene subjected to this treatment was recovered. Details of the experiment are as follows:-

Weight of nickel used = 14 grammes
Ratio - nickel : pumice = 1 : 4
Thiophene treated = 11·80 grammes
" recovered = 10·34 "
Rate of flow of thiophene = 10 grammes/hour
" " " " hydrogen = 10 litres/hour
Thiophene decomposed = 10-13%

On allowing the liquid air-cooled vessel to attain room temperature all the condensate was vaporised and collected over mercury. 250 cc. of gas were obtained, and on analysis gave the following figures:-

Hydrogen sulphide	0·7%
Unsaturated hydrocarbons	76·7%
Hydrogen	15·7%
Saturated hydrocarbons (butane)	4·9%
Undetermined	2·0%

Butane was identified by the quantity of carbon dioxide and water formed in the combustion of the residual gases. The unsaturated hydrocarbons were presumably butadiene, so that the decomposition may be represented thus:-

$$C_4H_4S + 2H_2 = H_2S + C_4H_6$$

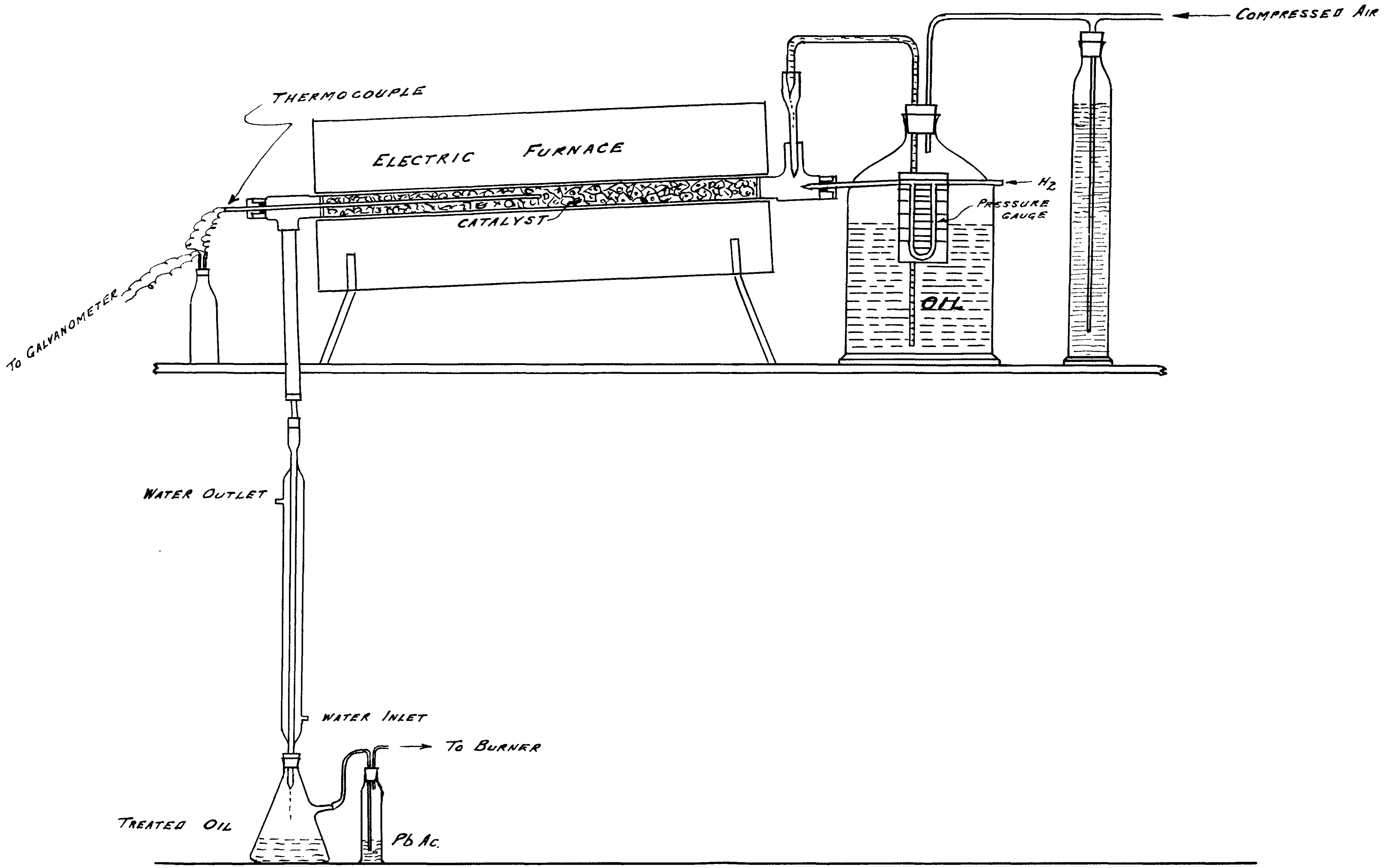
$$C_4H_6 + 2H_2 = C_4H_{10}$$

Conclusions.

Isoamyl sulphide was decomposed when brought into contact with the finely divided metals, nickel and iron, at 300°C. The former was the more active,, and again the presence of hydrogen greatly assisted the reaction.

Lime for this purpose proved of little use.

Thiophene was not appreciably broken down when subjected to nickel at 300° C., even in the presence of hydrogen. At 500°C. with hydrogen, thiophene was attacked, 10-13% being decomposed. Ring sulphur compounds offer much more resistance to attack than do thioethers.


COMPRESSED AIR
THERMOCOUPLE
ELECTRIC FURNACE
H_2
PRESSURE GAUGE
CATALYST
TO GALVANOMETER
OIL
WATER OUTLET
WATER INLET
TO BURNER
TREATED OIL
Pb Ac.

Deodorisation of Scotch Burning Oil by passing the Oil Vapour mixed with Hydrogen over finely divided Nickel on Pumice - Experiments conducted on a larger scale.

So far the process showing the greatest possibility of successfully removing the unpleasant odour from burning oil and, at the same time, having no bad effect on its colour, was that where the oil vapour and hydrogen were brought into contact with nickelised pumice at 300°C.-320°C. These experiments were now repeated on a slightly larger scale.

The apparatus, as shown by the accompanying sketch, consisted essentially of a reaction chamber containing the contact material with facilities at one end for the admission of hydrogen and oil, at the other end for removal of the products and introduction of a thermocouple. Here the reaction chamber was a cast-iron tube, three feet in length and 1½" in diameter, carrying at each end a T piece. The T piece at the inlet end had two packed glands, one for admitting the hydrogen, and the other for the oil, while that at the outlet side provided for placing a thermocouple in the centre of the furnace, and connecting a lead-off cast-iron pipe 18" long and ¾" diameter, by means of which the oil vapour and excess hydrogen were drawn off to a condenser and oil receiver. Hydrogen from a cylinder was stored in a small gas holder under a pressure of 6" of water, and from there led through a gauge to the reaction tube as required. The oil was forced by compressed air from a small container to a jet inside a perpendicular glass tube, which passed through the other gland at the inlet end of the tube. This method of feeding in the oil resulted in the fore part of the tube acting as a vaporising chamber. By this means it was hoped that, besides making the process continuous, a more true conception of the deterioration of the catalyst from the sulphur content of the various portions would be obtained than if a gallon or two gallon still had been used, and the distillate collected fractionally, since the higher boiling fractions contain the largest percentage of sulphur (52). To heat the reaction tube, an electric furnace 2'6" long and 2" internal diameter was constructed.

In preparing the catalyst, the "hydroxide method" used in the last experiments gave place to the more simple method of igniting the nitrate of nickel. In this case, to a concentrated solution of nickel nitrate containing 40 grammes of nickel was added 400 grammes of pumice, size about ½" cube. This mixture was evaporated to dryness with constant stirring, and then heated at about 300°C. to convert the nitrate to the oxide. The reaction tube was then packed with this product, and reduced with hydrogen at 300°C.-320°C

As soon as the oxide of nickel had been completely reduced, the oil was fed in at the rate of one litre per three hours, and the flow of hydrogen adjusted to give about 20% by volume of the oil vapour. The volume of oil vapour was calculated roughly, assuming a mean formula of the oil to be $C_{12}H_{26}$ (boiling point 215°C.), and also assuming its sp. gr. as 0·8. Thus 800 grammes or one litre of oil yield 107·9 litres vapour at N.T.P., and therefore 10% hydrogen in this case would be 10·79 litres per litre of oil.

Under these conditions, two gallons of burning oil were passed over the nickel on pumice at 300-310°C., and collected in portions of 500 cc. The sulphur content of every third portion is shown in Table XIV.

Below are details of the experiment:-

Weight of nickel = 30 gms. = 148 nickel nitrate
Ratio Nickel : Pumice = 1 : 10 approx.
Rate of distillation of oil = 1000 cc. per 3 hours or 159 cc. per sq. inch of cross section per hour.
Volume of oil distilled = 9000 cc.

TABLE XIV.

Distillate Portion No.	Sulphur %
1	0·109
4	0·120
7	0·120
10	0·120
13	0·120
16	0·125
18	0·119
Untreated oil	0·140

The oil obtained by this treatment was disappointing.

The colour of the oil was bad, being a light brown. It contained some finely divided matter in suspension and, as seen from the above figures, the amount of sulphur removed was very much less than in the previous experiments. The smell of the product was distinctly improved, and it was noted that the amount of sulphur removed was constant throughout the run. These two facts seem to point to the preferential decomposition of certain sulphur bodies, or class of bodies, and that this class is that having the most disagreeable odour.

Before going further with this series of experiments, it was decided to take the factors - colour, suspended matter, and non-removal of sulphur, find their cause and, if possible, eliminate them.

As regards the question of colour, it was suspected that it was due to the red lead of the jointing material (red lead and linseed oil) being dissolved in the oil. To investigate this, 500 cc. of the oil were distilled to small bulk, the residue transferred to a crucible, ignited, cooled and weighed, showing a residue of ·0106 grammes. This, on analysis, proved to contain lead. The colour of the distillate was good, so that the colour of the product under consideration appeared to be due to lead salts of one or more of the acids contained in linseed oil. This explanation was supported by the fact that when a paste of red lead and linseed oil was heated with burning oil, a reddish brown oil resulted. Red lead and linseed oil heated separately with burning oil did not affect its colour. Hereafter the jointing material consisted of a mixture of water-glass and fireclay.

The fine suspended matter contained in the first two and a half litres was allowed to settle for a few days, removed by filtration, and subjected to a qualitative examination. This showed it to consist of pumice, red lead, and a trace of nickel, all of which had been mechanically carried over into the receiver.

To account for the small amount of sulphur removed the following points were considered and examined:-

1. Method of vaporising the oil.
2. Method of preparing the catalyst.
3. Proportion of hydrogen to oil vapour.
4. Temperature.
5. Time of contact of oil vapour and catalyst.
    (a) Rate of flow of oil vapour.
    (b) Size of pumice carrier.
6. Proportion of nickel to pumice stone.

Method of vaporisation of oil.

1. The method adopted of feeding the oil into the reaction chamber was open to the objection that the oil was not vaporised before it reached the catalyst, so that only part of the catalytic material had been utilised. Had this been

the case the portion of the catalyst near the inlet end would contain less sulphur than that in the centre or outlet end of the tube. Analysis of the contact material cleared up this point.

The nickelised pumice was removed from the tube, roughly divided into three portions, (1) that from the fore part of the tube, (2) that from the centre and (3) that from the outlet end. Each portion was systematically sampled, ground, and the nickel and sulphur content of each determined. Table XV shows the results obtained:-

TABLE XV.

Portion	Nickel %	Sulphur %	Nickel:Sulphur
1.	8·51	·661	100 : 7·77
2.	7·24	·251	100 : 3·47
3.	7·58	·242	100 : 3·19

These figures are of the order to be expected if the oil were admitted as vapour, so it can safely be assumed thst if the oil is not vaporised before it reaches the catalyst, it is all converted to vapour before it has gone any appreciable distance.

At this point, a balance showing the sulphur removed from the oil compared with the sulphur absorbed by the nickel, may be of interest.

Sulphur combined with nickel.

Portion	Weight gms.	Sulphur %	Sulphur gms.
1.	136	·661	·661 x 1·36 = ·897
2.	106	·251	·251 x 1·06 = ·266
3.	98	·242	·242 x ·98 = ·238

Total sulphur combined with nickel = 1·40 gms.

Sulphur removed from oil.

Mean sulphur percentage removed from oil = 0·02

Volume of oil treated = 9,000 cc. = 7,200 gms.

∴ Total sulphur removed = 7,200x·0002

= 1·44 gms.

Method of preparation of catalyst.

II. On considering the two methods of preparing the catalyst, it was thought possible that in the "hydroxide method" used in the small scale experiments,the small amount of caustic soda remaining in the contact material,after even the most thorough washing,might act as a "promoter", thereby increasing the activity of the nickel. It was therefore decided to prepare some nickelised pumice by the "hydroxide method", and repeat the experiment detailed in pages 68-70. As described previously, this method consisted of dissolving a known qusntity of nickel nitrate, adding pumice, then caustic soda, and filtering off the mixture of nickel hydroxide and pumice, with subsequent reduction of the hydroxide. On a larger scale this would lead to the formation of a considerable quantity of nickel dust, which would probably be carried off with the hydrogen and oil vapour. To minimise this, the operation was slightly altered to the following:- pumice (size about ½" cube) was allowed to soak in a hot solution of nickel nitrate, removed, drained and steeped in a 10% caustic soda solution. It was then filtered off, washed, dried and reduced at 300°C. This mode of preparation, however, necessitated determining the exact strength of nickel nitrate solution required to give a definite proportion of nickel to pumice in the product. This was done by soaking small quantities (20 gms.) of pumice in nickel nitrate solutions of different strengths, precipitating the hydroxide on the pumice as above, and estimating the nickel contained in the nickel oxide-pumice mixture obtained by ignition of the hydroxide. The results of these experiments permitted of a graph being drawn showing the relation between the strength of nickel nitrate solution, and the proportion of nickel to pumice in the product.

In preparing the catalyst for the following experiments the strength of nickel nitrate solution used was 135 parts nickel nitrate per 100 cc. of solution, which gave in the product a proportion of 1 part nickel to 10 parts pumice.

Two gallons of burning oil were passed over the catalyst with hydrogen at 300°C., under exactly the same conditions as detailed on page 70. The product was collected in portions of 500 cc., and the sulphur content and iodine number of every third portion determined. The results are shown in Table XVI. Details of the experiment are as follows:-

Weight of pumice...... = 376 gms.
Weight of nickel...... = 38 gms.= 187 gms.nickel nitrate.
Rate of flow of oil... = 1,000 cc. per 3 hours, or 159 cc. per sq. inch of cross section per hour.
Volume of oil treated. = 9,000 cc.
Volume of hydrogen.... = 20% of oil vapour

TABLE XVI.

Portion No.	Sulphur %	Iodine No.
1	0·106	74·6
4	0·117	74·6
7	0·121	75·1
10	0·116	75·4
13	0·123	75·5
16	0·113	76·9
18	0·117	76·8
Untreated oil	0·141	76·8

The amount of sulphur removed, as shown in the above Table, was of the same order as when the catalyst was prepared by igniting the nitrate, and subsequently reducing the oxide. Here again, although the sulphur eliminated was only a very small proportion (14%) of the total sulphur in the oil, the smell of the oil was very much improved. The colour of the treated oil, while not water-white, was much better than that of the sample as received.

Proportion of hydrogen to oil vapour.

3. To ascertain the effect on the amount of sulphur eliminated from the oil of the concentration of hydrogen in the oil-hydrogen mixture, a few experiments were completed under exactly the same conditions as detailed above, except that the quantity of hydrogen used was varied. Table XVII shows the results obtained. The proportion of hydrogen was calculated as explained before, i.e. assuming a mean molecular formula for the oil of $C_{12}H_{26}$. This is perhaps a very rough measurement of the volume of oil vapour, but it is quite accurate enough for the purpose required here, and at least gives comparative figures.

TABLE XVII.

Oil	Hydrogen Pts/ 100 Pts. Oil Vapour	Sulphur content of Product.
1st 500 cc.	13	0·106
2nd "	37	0·113
3rd "	114	0·110
4th "	174	0·117

These figures demonstrated that an increase in the quantity of hydrogen used above 13 parts per 100 parts of oil vapour did not result in any increase in the amount of sulphur removed from the oil.

Temperature.

4. Similar experiments were carried out at 350°C. and

400°C. No improvement in the amount of sulphur eliminated was found, even at 400°C., while in the latter case the product had a distinctly green colour. Also at the higher temperature, the hydrogen burned with a faintly luminous flame, indicating that "cracking" had taken place to a small extent. The sulphur contents of the various products were:-

	Sulphur %
Oil treated at 300°C.	0·115
" " " 350°C.	0·115
" " " 400°C.	0·112
Untreated oil........	0·141

Time of contact of oil vapour and catalyst.

5. (a) Rate of flow of oil vapour.

Comparing these experiments with the small scale experiments (page 53) it was found that since the length of the reaction tubes were the same, the time of contact depends on the rate of flow of oil per square inch cross-section. This factor in the small experiment was 151 cc. per hour, while in the large experiment it was slightly greater, 189 cc. per hour.

(b) Size of pumice stone carrier.

The larger the size of the pumice stone, the less surface of the catalyst would be exposed, i.e. the shorter the time of contact of oil and catalyst. In the large scale experiment the size of the pumice stone was much larger (viz: to pass through ½" sieve as against ¼" sieve in the small experiment). By repeatedly passing the oil vapour and hydrogen over the catalyst the time of contact was increased. Two litres of oil were passed five times over the catalyst at 300°C., but no greater proportion of sulphur was removed. Little effect was noted in the iodine number of the product.

TABLE XVIII.

	Sulphur %	Iodine No.
Oil after 1st treatment...	0·115	75·0
" " 2nd " ...	0·111	74·5
" " 3rd " ...	0·110	74·5
" " 4th " ...	0·110	73·0
Untreated oil...........	0·141	76·8

(c) Repeated treatment of the oil having yielded no better results, the size of the pumice stone was now reduced to that used in the small scale experiments (i.e. to pass through ¼" sieve and be retained on $\frac{1}{8}$" sieve). All other factors were maintained as in No. 2. Two gallons of the oil were thus treated, and collected in portions of 500 cc. The iodine number and sulphur content of every third portion were determined. Results are shown in Table XIX. A distinct improvement in the amount of sulphur eliminated was obtained, but this was still considerably less than in the initial small scale experiment. In the latter case, 13 grammes of nickel reduced the sulphur content of one litre of oil from 0·148% to 0·055%, or approximately 66%, while here 40 grammes of nickel reduced the sulphur content of the first 3 litres from 0·140% to 0·093%, or approximately 34%. The smell of the treated oil was again much improved, while the colour was slightly better than that of the original oil.

TABLE XIX.

Portion	Sulphur %	Iodine No.
1	0·070	68·8
4	0·101	73·5
7	0·107	74·3
10	0·106	76·1
13	0·106	75·2
16	0·111	76·9
18	0·117	76·6
Untreated oil	0·140	76·8

Proportion of nickel to pumice stone.

6. Finally, the following experiment was carried out, in which the proportion of nickel to pumice in the contact material was increased from 1 to 10, to 1 to 4, while the size of the pumice remained as in the last experiment. As before, the oil vapour was passed with hydrogen over the nickelised pumice at 300°C., and every 500 cc. collected separately. Table XX gives particulars of the experiment, and shows how the catalyst was affected. The first six litres showed a decided increase in the amount of sulphur

eliminated. Compared with the small scale experiments, the results were only moderately satisfactory - a decrease of 45% of the total sulphur as against 66%. The experiment was proceeded with until the nickel was exhausted, i.e. until hydrogen sulphide appeared in the outgoing gas. The details of the experiment were as under:-

TABLE XX.

Weight of nickel - 74·7 gms. - 363 gms. nickel nitrate
(or 2·6 ozs. - 12·8 ozs.)

Ratio nickel:pumice - 1 : 4

Size of pumice - passed through a ¼" sieve and retained on ⅛" sieve.

Temperature - 300°C.

Volume of hydrogen - 10%-20% of oil vapour.

Volume of oil - 85·5 litres or 19 gallons.

Volume of Oil - gals.	No. of Portion	Sulphur %	Iodine No.
0	1	0·049	58·0
	4	0·082	-
	7	0·081	71·4
1	10	0·099	-
	13	0·082	74·5
	16	0·071	-
2	19	0·091	74·4
	22	0·104	-
	25	0·094	76·7
3	28	0·097	-
	31	0·088	74·8
	34	0·094	-

(Contd.)

TABLE XX (Contd.)

Volume of Oil - gals.	No. of Portion	Sulphur %	Iodine No.
4	37	0·100	79·6
	40	0·095	-
	43	0·102	79·2
5	46	0·094	-
	49	0·095	-
	52	0·087	-
6	55	0·084	81·6
	58	0·095	-
	61	0·101	78·2
7	64	0·098	-
	67	0·092	82·4
	70	0·100	-
8	73	0·107	81·3
	76	0·094	-
	79	0·110	80·4
9	82	0·091	-
	85	0·093	82·7
	88	0·097	-
10	91	0·104	80·6
	94	0·100	-
	97	0·096	80·3
11	100	0·102	-
	103	0·098	80·0
	106	0·096	-
12	109	0·108	79·5
	112	0·109	-
	115	0·103	81·2
13	118	0·107	-
	121	0·099	83·0
	124	0·099	-

(Contd.)

TABLE XX (Contd.)

Volume of Oil - gals.	No. of Portion	Sulphur %	Iodine No.
14	127	0·099	-
	130	0·112	-
	133	0·102	82·5
15	136	0·114	-
	139	0·112	-
	142	0·107	-
16	145	0·104	83·0
	148	0·105	-
	151	0·116	82·0
17	154	0·093	-
	157	0·117	84·3
	160	0·105	-
18	163	0·112	83·3
	166	0·113	-
	169	0·112	-
19	172	0·096	83·9
	172 after soda wash	0·095	
Untreated oil used in first 5 gals..........		0·139	82·8
Untreated oil used in last 14 gals..........		0·127	84·0

During the treatment of the first two gallons the efficiency of the catalyst as a desulphurising agent gradually decreased. From this point until the 16th gallon had been treated the amount of sulphur removed was practically constant. Unfortunately, after the 5th gallon a fresh supply of oil had to be obtained, and this had a lower sulphur content, viz: 0·127%, so that now Table XX shows a decrease in sulphur, while actually it is of the same order. So far, the smell of the product had been very good, although the amount of sulphur eliminated was only 20% of the total sulphur content of the oil. After the 15th gallon, however, hydrogen sulphide was detected in the escaping hydrogen, and the oil had a distinct smell of the former gas. A caustic soda wash, whilst making no appreciable difference to the sulphur content of the last four gallons, removed this smell, leaving the oil with much the same smell as the first 15 gallons. The colour of the treated oil was better than that of the original sample, but after ten days' exposure to diffused light, it became slightly worse than the original oil. On standing for two months in diffused light, the colour was very much better than that of the untreated oil subjected to a similar exposure.

Conclusions.

Raising the temperature of the contact chamber to 400°C. yielded no further increase in the amount of sulphur removed from the oil, but on the other hand, resulted in a slightly coloured product. Signs of cracking were noticeable at the higher temperature.

The efficiency of the catalyst was greatly increased by -

(1) reducing the size of the pumice stone carrier
(2) increasing the proportion of nickel to carrier

It was demonstrated that while only a small proportion of the total sulphur was removed, the smell of the oil was good. The unpleasant smell appears therefore to be a property of a small proportion of the sulphur compounds, and further, that these compounds are more easily attacked than the remaining sulphur bodies.

From the presence of hydrogen sulphide in the outgoing gas towards the end of the run it was presumed that the metallic nickel had all been converted to the sulphide, and since the process proceeded unretarded, nickel sulphide itself must be capable of acting catalytically in the destruction of certain sulphur bodies.

Decomposition of organic sulphur compounds by a nickel sulphide catalyst.

The assumption that nickel sulphide acts as a catalyst in decomposing certain sulphur bodies was now investigated. Again, isoamyl sulphide and thiophene represented thioethers and ring sulphur compounds respectively. In preparing the nickel sulphide, however, it was found that the higher sulphides of nickel were reduced to the subsulphide at 300°C. Two methods of preparing the nickel sulphide catalyst resulted in the same product, Ni_3S_2.

(1) An ammoniacal solution of nickel chloride containing granulated pumice was saturated with H_2S, and the resulting sulphide filtered off and dried in an atmosphere of hydrogen at 120°C. The dry sulphide was packed in a combustion tube, and heated in a current of hydrogen to 300°C. At 200°C. hydrogen sulphide appeared with the excess hydrogen, and as the temperature rose, the volume of this gas formed increased. After maintaining the temperature of the catalyst at 300°C. for twelve hours, the outgoing gas still contained traces of hydrogen sulphide. On analysis the product was found to contain 16·42% nickel and 6·65% sulphur, or 71·2 parts Ni to 28·8 parts S. The subsulphide of nickel, Ni_3S_2, requires 73·3 parts Ni to 26·7 parts S. The higher sulphide has therefore been almost

entirely reduced to the lower sulphide.

(2) Nickel oxide on pumice, prepared by ignition of the nitrate, was converted to the sulphide by hydrogen sulphide at 200°C. This was reduced by hydrogen at 300°C. The product again was the subsulphide. The progress of the reaction was followed by periodically estimating the hydrogen sulphide content of the outgoing gas - Table XXI. The method of estimation of hydrogen sulphide adopted was to pass the gas through an ammoniacal solution of cadmium chloride, collect the cadmium sulphide, wash this into a standard iodine solution, and then titrate the excess iodine with thiosulphate.

Analysis of the product after 24 hours' reduction gave 16·73% Ni, 6·57% S or 71·81 parts Ni to 28·19 parts S.

TABLE XXI.

Nickel 18 gms. : pumice 52 gms. : speed of hydrogen 13·2 litres per hour.

Time from commencement of reduction of nickel sulphide.	H_2S in outgoing gas m. gms. per litre
1 hour	45·0
2 hours	30·0
3 "	29·0
5 "	21·0
9 "	11·0
12 "	5·4
16 "	0·63
20 "	0·17
24 "	0·14

That the particular sulphide of nickel formed by passing hydrogen over nickel oxide at 300°C. was the tetrasulphide, Ni_3S_4, and that this sulphide was reduced by hydrogen at 300°C. to the subsulphide, N_3S_2, and no further, was demonstrated as follows:-.

A small quantity of nickel oxide on pumice (4 gms. pumice to 0·16 gms. nickel) was packed in a small combustion tube, and heated in an electric furnace for six hours, while hydrogen sulphide, dried over phosphorous pentoxide, passed through the tube. The temperature was again measured by a thermocouple embedded in the pumice stone. At the end of this period the product was allowed to cool in an atmosphere of hydrogen sulphide, and when cold this gas was swept out of the tube by hydrogen. Analysis of the catalyst so obtained gave 3·37% nickel and 2·37% sulphur, or 58·7 parts Ni to 41·3 parts S. A similar experiment where finally, before cooling, the tube was cleared of hydrogen sulphide and filled with nitrogen, yielded a product containing 3·77% Ni and 2·65% S, or again 58·7 parts Ni to 41·3 parts S.

Nickel tetrasulphide, Ni_3S_4, contains 57·8 parts Ni to 42·2 parts S.

The reduction of the tetrasulphide was carried out in the same apparatus. A small quantity of nickel oxide was converted to the sulphide, and then reduced with hydrogen at 300°C. The outgoing gas was examined periodically, showing the progress of the reduction - Table XXII.

TABLE XXII.

Weight of nickel ....= 0·38 gms.
Weight of pumice ....= 8·00 gms.
Rate of flow of hydrogen..= 12 litres per hour.

Time from commencement of reduction of Ni_3S_4		H_2S in outgoing gas m. gms. per litre
20 mins.	....	13·4
50 "	....	11·2
90 "	....	1·67
3 hours	....	0·39
9 "	....	0·06
14 "	....	0·03
26 "	....	0·03
32 "	....	0·02
38 "	....	0·03

The concentration of hydrogen sulphide in the outgoing gas after 14 hours was reduced to 0·03 m. gms. per litre, and at this figure it remained for 24 hours. The reduction was then discontinued. An analysis of the product showed it to contain 5·72% nickel and 2·20% sulphur, or 72·2 parts nickel to 27·8 parts sulphur, again approximating the composition of nickel subsulphide. The rate of reduction during the last 24 hours was so slow that it may be assumed for all practical purposes that the reduction of the higher sulphide of nickel proceeds no further than the subsulphide, Ni_3S_2.

Recently, Evans and Stanier (55), while studying the removal of carbon disulphide from coal gas by the Carpenter process, found that the system, $Ni_3S_2 + 2 H_2 = 3 Ni + 2 H_2S$, was in equilibrium at 420°C. when the concentration of hydrogen sulphide in the gaseous mixture was 2-3 grains per 100 cb. ft. (0·04 - 0·06 m. gms. per litre) ~~per litre~~ of hydrogen.

The existence of the sulphides, Ni_3S_2, Ni S and Ni_3S_4, has been proved by Bornmann (53), while Dewar and Jones (54) prepared the subsulphide by the action of sulphur, in carbon disulphide solution on nickel carbonyl.

Isoamyl sulphide.

The behaviour of isoamyl sulphide, on being vaporised and passed with hydrogen over the subsulphide of nickel at 300°C., was now studied. Pure, dry hydrogen was passed through a gauge, and thence through a flask containing heated isoamyl sulphide. The mixture of isoamyl sulphide vapour and hydrogen was then led through a tube containing nickel subsulphide on pumice maintained at 300°C. The products of decomposition were forced through a water condenser to an ice-cooled receiver, and then to a receiver cooled by liquid air. From this, the hydrogen was led off and burned. Below are particulars of the experiments:-

Weight of isoamyl sulphide subjected to above treatment..= 16·76 gms.

Weight of isoamyl sulphide recovered......................= 1·33 gms.

Weight of nickel in catalyst....= 18·00 gms.

Ratio of nickel to pumice.......= 1 : 4

Length of reaction tube.........= 2'6" and dia. $\frac{3}{4}$"

Rate of flow of hydrogen........= 10 litres per hour

Rate of flow of isoamul sulphide= 10 gms. per hour

Isoamyl sulphide decomposed.....= 15·43 gms.

Only the unchanged isoamyl sulphide collected in the first receiver, while that cooled by liquid air contained a colourless liquid. The gas boiling off from this receiver at room temperature was collected, examined and found to consist of:-

Hydrogen sulphide........80·4%
Unsaturated hydrocarbons.17·5%
Residue (hydrogen)....... 2·1%

The remaining liquid was unsaturated, and boiled between 30-34°C., and so probably consisted of isoamylene with a small quantity of isopentane. On bromination at -10°C. the liquid was converted entirely to dibrompentane, 72% being the particular isomers boiling between 170 and 180°C. (Found Br = 69·1%: $C_5H_{10}Br_2$ reqd 69·5% Br.). This indicated the absence of pentane. The probability of pentane being brominated at the temperature was entertained, but 50 cc. of pentane subjected to the above treatment yielded only two drops of a brom derivative.

The complete course of the decomposition may now be written:-

1. $(C_5H_{11})_2S = 2\ C_5H_{10} + H_2S$
2. $Ni_3S_2 + H_2S = 3\ NiS + H_2$ and $NiS + H_2S = Ni_3S_4 + H_2$
3. $Ni_3S_4 + H_2 = 3NiS + H_2S$ and $3NiS + H_2 = Ni_3S_2 + H_2S$

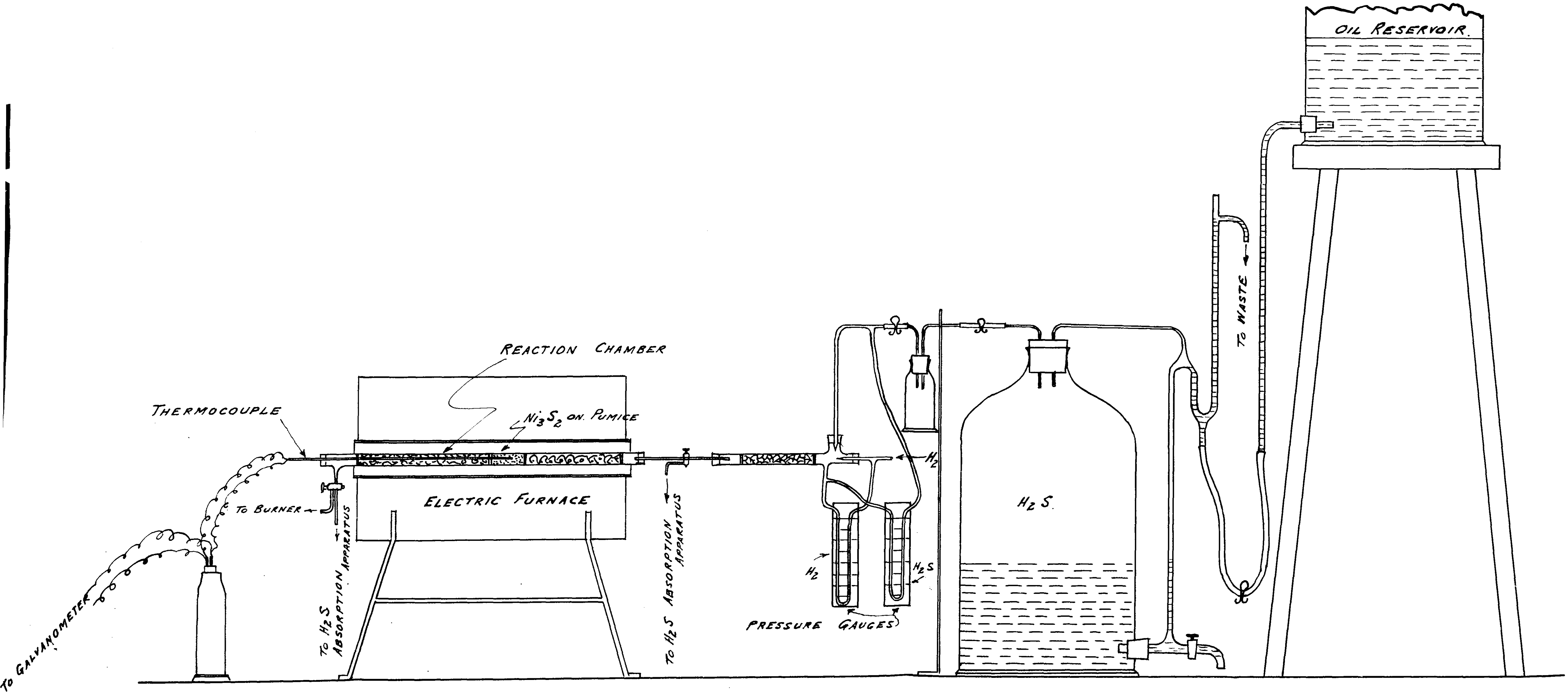
Apparently, the lower nickel sulphides as well as nickel act as catalysts in this decomposition of alkyl sulphides. At 300°C., however, the subsulphide cannot be reduced further. When metallic nickel is used, the first step is the formation of this sulphide, so that nickel subsulphide can be regarded as the compound which ultimately becomes the catalyst, no matter whether the metal or its sulphide is the starting material. The reaction, therefore, depends on the alternate formation of the higher sulphides of nickel and their reduction. Evans (55) goes further, and states that the velocity of the interaction of carbon disulphide and hydrogen is governed by the rate of reduction of the nickel sulphide formed.

Thiophene.

Attempts to decompose thiophene by passing the vapour mixed with hydrogen over nickel subsulphide under exactly the same conditions as affected the destruction of the thioether met with no success. This again supports the view that ring sulphur compounds are more stable towards the above treatment than open chain compounds. Fürth and Jaenicke (56) lately, while investigating the desulphurisation of lignite tar benzine, have been led to the same conclusion.

Nickel sulphides and their reduction.

It has been demonstrated that nickel subsulphide cannot be reduced further by hydrogen at 300°C., while the higher sulphides, NiS and Ni_3S_4, are readily reduced at this temperature to the lowest sulphide. This subsulphide has been proved to act as a catalyst in decomposing alkyl sulphides. It follows that if the rate of flow of hydrogen was adjusted so that the proportion of hydrogen sulphide to hydrogen did not become greater than the concentration of hydrogen sulphide required to maintain the system - hydrogen, hydrogen sulphide and nickel subsulphide in equilibrium at 300°C., then the decomposition of the sulphur compound would proceed evenly and regularly. The object of the following experiments was to determine this concentration of hydrogen sulphide when the above system was in equilibrium at 300°C., i.e., to determine the maximum amount of hydrogen sulphide which the hydrogen -


OIL RESERVOIR
TO WASTE
REACTION CHAMBER
THERMOCOUPLE
Ni_3S_2 ON PUMICE
TO BURNER
ELECTRIC FURNACE
TO H_2S ABSORPTION APPARATUS
TO H_2S ABSORPTION APPARATUS
H_2
H_2S
H_2
H_2S
PRESSURE GAUGES
TO GALVANOMETER

hydrogen sulphide mixture may contain, so that when the gas was passed over nickel subsulphide at 300°C. the last named would remain unchanged.

The method adopted was to pass various mixtures of hydrogen and hydrogen sulphide over nickel subsulphide deposited on pumice, and maintained at a temperature of 300°C. for a period of 8 to 10 hours. The catalyst was then analysed, and the ratio of nickel to sulphur calculated.

The apparatus used is shown opposite, and may be described briefly as follows:- About 4 gms. of nickel oxide on pumice (25 parts pumice to 1 part nickel, and of such size as to pass through an $\frac{1}{8}$" sieve and be retained on $\frac{1}{16}$" sieve) were placed in the centre of a glass tube 18" long and of $\frac{1}{2}$" diameter, and held in position by two asbestos plugs. The whole was heated in an electric furnace 14" in length. The inlet end of the tube was connected to a small mixing chamber to which hydrogen and hydrogen sulphide were supplied through glass jets. These jets were set at right angles to each other so that the gas from one jet was directed at that issuing from the other. Both jets were connected to pressure gauges which had been calibrated, so that the pressure recorded indicated approximately the volume of gas passing through the jets. The hydrogen was stored in a gasholder of the ordinary type, while the hydrogen sulphide was confined in an aspirator over heavy oil. The apparatus used for keeping the hydrogen sulphide under constant pressure throughout the experiment was a modification of that used by Dobson (57) for collecting a gas at constant pressure. A three-way stop cock, fixed between the mixing chamber and the tube containing the catalyst, allowed the gas to be by-passed through wash bottles containing cadmium chloride. By this means, the sulphur content of the gas could be determined, if required, immediately before the gas entered the reaction chamber. After passing over the catalyst the gases were led to a small burner and ignited. At this end also, there was an arrangement which permitted of the outgoing gases being analysed, when desired, without interrupting the experiment. The temperature was recorded by a nickel-nichrome thermocouple embedded in the catalyst.

The experiment itself was carried out as follows:- Nickel subsulphide was formed by first subjecting the nickel oxide to hydrogen sulphide, and then reducung the higher sulphide of nickel with hydrogen. The tube was then closed by turning the stop cocks at either end. The rates of flow of hydrogen and hydrogen sulphide to give the required mixture, were adjusted roughly by means of the gauges connected to each jet; the exact composition of the mixture was determined by estimating its content of hydrogen sulphide. When the proportion of hydrogen to hydrogen sulphide was constant, as indicated by analysis, the mixture of gases was allowed to pass over the catalyst, which, of course, had been maintained at 300°C. throughout. Under these conditions the experiment proceeded for 8 - 10 hours, its progress being followed by determining the hydrogen sulphide content of the outgoing gas periodically.

At the close of each experiment the tube was closed and allowed to cool, when the catalyst was removed, analysed and the ratio of nickel to sulphur calculated. It was very difficult, however, to construct a jet small enough to deliver less hydrogen sulphide than 100 cc. per hour, i.e. the speed required to give 10 parts per 1,000 parts of hydrogen; therefore for the lower concentrations of hydrogen sulphide, a mixture of hydrogen and hydrogen sulphide - not the latter alone - was delivered through the small jet. The main supply of hydrogen, as before, entered by the large jet. Table XXIII shows the results of a series of experiments where the proportion of hydrogen sulphide to hydrogen varied from 5 parts per 10,000 to 13·6 parts per 1,000. In each experiment about 4 grammes of contact material containing 4% of nickel were used.

TABLE XXIII.

Rate of flow of hydrogen. = 11 litres per hour
Weight of nickel......... = 0·16 gms.
Weight of pumice......... = 4 gms.

Pts. H_2S per 1000 pts. H_2	Anal. of product		Ratio	Nickel sulphides (theor)	
	% Ni	% S	Ni : S	Formula	Ratio Ni : S
Pure hydrogen	5·72	2·20	72·2:27·8	Ni_3S_2	73·3:26·7
0·5	3·74	1·66	69·3:30·7		
2·0	4·02	1·73	69·9:30·1		
5·0	3·54	1·94	64·6:35·4	NiS	64·7:35·3
13·7	3·16	1·83	63·3:36·7		
Pure H_2S	3·77	2·65	58·7:41·3	Ni_3S_4	57·8:42·2

When the concentration of hydrogen sulphide was more than 13·6 parts per 1,000 parts of hydrogen, the product of passing this mixture over the nickel subsulphide was the tetrasulphide Ni_3S_4. Between this concentration and 5 parts per 1,000 the normal sulphide NiS was stable, while below 2 parts per 1,000 the subsulphide was gradually formed.

Conclusions.

At a temperature of 300°C.

(1) hydrogen sulphide reacted with nickel oxide to form the tetrasulphide Ni_3S_4.

(2) hydrogen reduced this sulphide to the subsulphide so that the reactions

$$\text{(a)}\ Ni_3S_4 + H_2 = H_2S + 3\,NiS$$

$$\text{(b)}\ 3\,NiS + H_2 = H_2S + Ni_3S_2$$

are reversible, the trend of the reaction depending on the proportion of H_2S and hydrogen present.

When the gaseous mixture contained less than 2 parts of hydrogen sulphide per 1,000 parts of hydrogen, reaction (b) proceeded from left to right, but when the concentration of hydrogen sulphide was above 5 parts per 1,000, the action was reversed. Finally, at concentrations of hydrogen sulphide greater than 13·6 parts per 1,000 the tetrasulphide was formed according to (a) - right to left.

Isoamyl sulphide was decomposed when brought into contact with nickel subsulphide at 300°C. in the presence of hydrogen at 300°C., yielding isoamylene amd hydrogen sulphide. The latter combined with lower sulphide to form one of the higher sulphides depending upon the proportion of hydrogen to hydrogen sulphide present. If the volume of hydrogen be such that the concentration of hydrogen sulphide is less than 2 parts per 1,000, it follows that the catalyst would remain unchanged, and the desulphurisation of the thioether would proceed evenly and unretarded.

GENERAL CONCLUSIONS.

The conclusion is drawn that sulphur compounds, not unsaturated hydrocarbons, are responsible for the characteristic smell of the burning oil fraction of shale oil. While no individual sulphur compound has been isolated, evidence points to the unpleasant smell being due to the small percentage of the sulphur present as open chain compounds of the thioether type. This class of body forms crystalline odourless addition compounds with mercuric chloride, is oxidised to sweet smelling sulphoxides, and possibly sulphones, and is decomposed by contact with nickel or its lower sulphides at 300°C. These three properties of the alkyl sulphides form the basis of three processes which were successful in deodorising the oil.

1. Treatment of the oil with mercuric chloride certainly destroys its unpleasant smell, presumably by forming addition compounds with the odoriferous sulphur bodies. Such a process, however, becomes impracticable when it is considered that (a) mercury chloride is slightly soluble in the oil, as is also, though to a less extent, the addition compound (b) the addition compound breaks down into the thioether and mercury chloride at temperatures little over 110°C.

2. Burning oil, when agitated with certain oxidising

agents,-potassium dichromate and sodium hypochlorite- in the cold, loses its characteristic smell. The sulphur compounds, however, are not destroyed but merely oxidised to the odourless sulphoxides and sulphones which decompose, under the influence of heat,with the formation of evil smelling products. The sulphoxides and sulphones formed from the sulphides distilling between the temperatures 150 and 300°C. are not removed by a soda or water wash. These mild oxidising agents do not seriously attack the unsaturated hydrocarbons - indeed the loss of oil during the process does not exceed 3%. The character of the oil remains unchanged; the distillation range, specific gravity tests and iodine number determinations of the treated and untreated oils are almost identical. An examination of oil for (OH) groups gave negative results. The hypochlorite treated oil after filtration through bauxite contained only 0·02% chlorine. With both oxidising agents the colour of the product, however, was adversely affected, but by filtering the treated oil through bauxite an oil of good colour resulted. This process therefore, appears to offer a possible method of deodorising the burning oil, provided there is no necessity for distilling the oil subsequently.

3. Certain sulphur compounds are decomposed when brought into contact with metallic nickel or its subsulphide in the

presence of hydrogen at 300°C.

Using nickel as catalyst

isoamyl sulphide, a typical open chain compound, is almost completely decomposed yielding isopentane, isoamylene, and hydrogen sulphide thus:-

$$(C_5H_{11})_2 S + H_2 = C_5H_{10} + H_2S$$

$$C_5H_{10} + H_2 = C_5H_{12}$$

thiophene, a closed ring compound, at 300°C. is but slightly affected, but at 500°C. 10-15% of thiophene is destroyed with the formation of butane, hydrogen sulphide and presumably, butadiene.

$$C_4H_4S + 2H_2 = C_4H_6 + H_2S$$

$$C_4H_6 + 2H_2 = C_4H_{10}$$

Nickel subsulphide, however, does not bring about the decomposition of thiophene at 300°C., but effects the desulphurisation of isoamyl sulphide

$$(C_5H_{11})_2S + H_2 = C_5H_{10} + H_2S$$

The hydrogen sulphide evolved converts metallic nickel and its lower sulphides to the tetrasulphide, Ni_3S_4. This, however, is reduced to the subsulphide, Ni_3S_2, by hydrogen. Further reduction, if it does take place, is so slow as to be negligible. The catalytic action, therefore, depends on the formation and subsequent reduction of the higher sulphides of nickel. Thus, no matter whether metallic nickel or its sulphide is initially the catalyst, the subsulphide ultimately becomes the agent, provided the rate of flow of hydrogen is adjusted so that the hydrogen sulphide content of the hydrogen, hydrogen sulphide mixture is kept less than the concentration required to maintain the system,

$$Ni_3S_2 + H_2S = 3NiS + H_2 \text{ in equilibrium at } 300^\circ C.$$

This concentration was found to be 2 parts of hydrogen sulphide per 1,000 parts of hydrogen. A process by which, if carried far enough, the sulphur bodies could be completely eliminated, consists in bringing the oil into contact with nickel in presence of hydrogen at 300°C. Complete desulphurisation, however, is not necessary to deodorise the oil. The smell of the oil is due to certain sulphur bodies which are readily decomposed when brought into contact with nickel or its subsulphide at the above temperature. Metallic nickel is the more active catalyst in removing sulphur from the oil, but its subsulphide efficiently brings about the decomposition of those sulphur bodies which are responsible for its characteristic smell. The inference again is drawn that this smell is a property of certain open chain sulphur compounds, while the more stable ring compounds are comparatively harmless.

This catalytic process of decomposing the odoriferous constituents of burning oil has so far given the most satisfactory results.

In practice, the burning oil vapour from the final distillation could be led with hydrogen through a chamber containing nickelised pumice maintained at 300°C. The oil would be collected in the usual way, while the hydrogen, after passing through a hydrogen sulphide purifier, would be drawn to a gasholder and re-circulated. The deodorising action would proceed continuously if the flow of hydrogen were adjusted so that the concentration of hydrogen sulphide in the reaction chamber did not exceed 2 parts per 1,000 parts of hydrogen.

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PATENTS ON THE ELIMINATION OF SULPHUR FROM HYDROCARBON OILS.

The patents in the following list are classified according to the active desulphurising agents employed; the method of applying these agents is indicated.

AMMONIA.

Lucas, Palmer and Perkin - B.P.108,019 of 17/7/16.
Oil, as liquid, is heated with ammonia above its boiling point under pressure.

Freeman - B.P. 193,979 of 5/12/21.
Oil is atomised and heated with ammonia with or without hydrogen.

Glancy - Oil is treated with liquid anhydrous ammonia.
(A) U.S.P. 1423710 (B) 1423711 (C) 1423712 of 25/7/22.
(B) refers to recovery of sulphur compounds.
(C) refers to use of steam.

Lucas and V.L. Oil Processes Ld. - International Specification 211664 - Application date 19/1/23. This is an improvement on E.P. 108019.
Sulphur compounds are extracted by successive treatments with liquid anhydrous ammonia, and the product drawn off after each treatment.

Arnold - U.S.P. 1454593 of 8/5/23.
Oil is treated with liquid anhydrous ammonia in presence of an alkali metal oxygen bearing compound.

BAUXITE, FLORIDIN AND THE LIKE.

Hood - B.P. 145818 of 24/2/19.
Oil is vaporised and brought into contact with alumina, bauxite or magnesite.

McCrae - B.P. 141272 of 8/9/19.
Vapour of the hydrocarbon is brought into contact with bauxite clay or the like.

Dunstan and Remfry - B.P. 190553 of 28/9/21.
Oils are treated with floridin followed by bauxite treatment.

Remfry - E.P.212500 - 1924 - Bauxite as a refining agent.

PATENTS (Contd.)

HYDROGENATION with and without catalysts.

Bergius - G.P. 30/11/13. no 290,563

Hydrocarbons are heated above 200°C. under pressure with hydrogen in presence of metallic oxides and hydroxides. Pressure is sufficient to keep hydrocarbon liquid.

Badische Anilin und Soda Fabrik - Fr,P. 472771 of 28/5/14.

Oil is heated not above 200°C. and treated in fluid condition with hydrogen in presence of a catalyst such as nickel, cobalt, iron and copper.

Greesham - Fr.P. 473110 of 5/6/14.

Oils, resins or rubbers treated with molecular hydrogen with or without pressure are desulphurised.

Evans - B.P. 22147 of 6/11/14.

Oil is vaporised, mixed with hydrogen and passed over a catalyst such as nickel on fireclay.

Bullinger, Melhardt, Winternitz and Zerner - International Specification - Application date 14/6/23 No. 218989.

Oil is heated in fluid phase at 300°C. under pressure of 10 atmospheres in presence of an absorbent carrier containing nickel with or without cobalt, iron or copper.

Lucas and V.L. Oil Processes Ld. - B.P. 214817 - Application date 21/6/23.

For removing unsaturated compounds. The oil is vaporised and passed with hydrogen (containing ·01 -·015 parts chlorine or bromine) through a filtering and polymerising medium - floridin, bauxite etc.

Forwood and Tapley - B.P. 133059 of 12/12/16.

Oil vapour is mixed with steam and brought into contact with carbon at 450-600°C. to form nascent hydrogen.

METALS.

Hutz - G.P. 374928 of 15/12/20.

Mineral or tar oils are purified from sulphur by heating with metallic sodium.

Rudge and Hodgkinson - B.P. 6479, 14424, 14425, 17585 of 4/3/22.

Oil in vapour or liquid state is brought into contact with copper, zinc, iron or their oxides, halides or oxyhalides.

PATENTS (Contd.)

METALLIC CHLORIDES.

Heyl - B.P. 115452 of 1917.

Shale oils are obtained free from sulphur by mixing with the shale before distilling it a sufficient quantity of ferric chloride to combine with all the sulphur in the shale.

Dey - U.S.P. 1365894 of 18/1/21.

Oil is desulphurised by being brought into contact with cuprous chloride.

METALLIC OXIDES AND HYDROXIDES.

Frasch - J.S.C.I. 1912 - 169. U.S.P. 378246 of 1888.

The oil is distilled with two or more oxides of the following metals - lead, bismuth, cadmium, mercury, copper, silver, manganese, iron, tin, nickel, cobalt, or zinc.

Smith - B.P. 153844 of 14/4/20.

Oils are freed from sulphur and phosphorous by heating in a closed vessel with cotton waste or other absorbent material containing 1-5% solution of alkali hydroxide - pressure 100-150 lbs. per square inch.

Neilson and Hutton - B.P. 153857 of 20/5/20.

Washing of the oil, after heavy acid treatment, with alkali is facilitated by the addition of a small quantity of a sulphonated fatty acid.

Benson - B.P. 170013 of 10/7/20.

Sulphur is removed from oil by heating with quick lime under a pressure of 100 lbs. per square inch, and sufficient superheated steam to raise temperature to 120°C.

METALLIC SULPHIDES.

Cobb - U.S.P. 1413005 of 18/4/22 and U.S.P. 1300816 of 15/4/19.

Oil is agitated with monosulphides of alkali or alkali earth metals - this process removes free sulphur.

Hood - B.P. 129349.

Oil is agitated with a solution of alkali or alkali earth sulphides at atmospheric temperature of 40°C.

R. Pachon - G.P. 380059 of 4/6/21.

Shale oil is desulphurised when vaporised and passed over a lower sulphide of a metal capable of forming a higher sulphide.

PATENTS (Contd.)

ORGANIC COMPOUNDS.

Deutsche Erdöl - G.P. 357768.

Oils are treated with alcohol to which has been added sufficient water to cause the separation of a layer which contains the coloured, odourous, resinous and asphaltic matter. Oil is subsequently refined with alcoholic solutions of acids and alkalis.

also G.P. 352917 of 18/2/21.

Oil is treated with 5% of paraffin carboxylic acids or their halogen derivatives or anhydrides.

Hillman -

Uncombined sulphur is removed by treatment with an organic substituted hydrogen sulphide compound or a mercaptan.

Nelson - B.P. 113131 of 6/2/17.

Oil is treated with an unsaturated fatty oil such as linseed or cotton rape, with or without phosphoric acid.

OXIDISING AGENTS.

A. and L.O. Brin - B.P. 10968 of 1896.

Oil is treated with oxygen, ozone, or chlorine gas in order to decolorise and desulphurise it.

H.A. Frasch - U.S.P. 525811 of 1894.

The oil is agitated with a suspension of chloride of lime or bleaching powder, followed by sulphuric acid and sodium plumbite.

Dunstan - B.P. 139233 of 3/6/18 and 13515 of 12/5/21.
B.P. 201223 of 22/4/22 and 204078 of 22/4/22.

The oil is treated with a solution of alkali hypochlorite, free alkali being restricted within certain narrow limits.

Thole and Card - B.P. 231944 of 11/1/24.

Destabilisation of hypochlorite solution by CO_2 or salts of iron, manganese, magnesium or zinc.

Nesfield - B.P. 183527 of 14/6/21.

Oil is treated in thin film with chlorine gas.

Walkey and Bargate - B.P. 186738 of 18/7/21.

Oil is vaporised in presence of steam and gaseous dissociating agent, e.g. chlorine.

PATENTS (Contd.)

OXIDISING AGENTS (Contd.)

DEMOULINS ~~Demartins~~ - B.P. 216918 of 7/2/23.
Oil in vapour phase is subjected to the oxidising effect of hypochlorite.

SULPHUR DIOXIDE.

Edeleanu - B.P. 11140: J.S.C.I. 1908 - 974.
Extraction of sulphur compounds with liquid sulphur dioxide.

Walkey and Bargate - B.P. 186738 of 18/7/21.
Oil is vaporised in presence of steam and a gaseous dissociating agent, e.g. sulphur dioxide.

Hall - B.P. 26756 of 21/11/13.
Shale oil is charged with sulphur dioxide and distilled: subsequently subjected to Frasch process.

MISCELLANEOUS.

Nesfield - B.P. 196680 of 25/1/22.
Mineral oils are desulphurised by treatment with hydrochloric, mixed with air or hydrogen, washed with sodium or calcium hydroxide, and finally filtered.

Heyl - B.P. 213946 of 7/9/23.
Mineral oil is desulphurised by subjecting it to the action of an electric current traversing an aqueous solution of a metallic salt, e.g. caustic soda or sodium chloride. The oil may be emulsified with the brine - a metallic catalyst is precipitated in the pores of coke packed between the electrode plates.
