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PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Improvements in or relating to the Manufacture of Lubricating Oils

We, ARTHUR PEVERALL LOWES, of 154, Liverpool Road, Widnes, Lancashire, and DOUGLAS ELWOOD WHITE, of 24, Beaconsfield Crescent, Widnes, Lancashire, both British Subjects, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention to be as follows:—

This invention relates to improvements in the manufacture of synthetic lubricating oils.

It is well known that oily materials suitable e.g. as lubricants or as pour point depressants for lubricating oils can be prepared by condensing chlorinated hydrocarbons of high molecular weight with aromatic hydrocarbons such as benzene or toluene, in the presence of a condensing agent such as aluminium chloride. Such condensations are frequently effected in the presence of inert diluents such as kerosene or benzine. The products of such condensations separate usually into two layers, the upper one of which comprises the greater part of the oily material, together with the diluent and a very small fraction of the condensing agent, and can be worked up by vacuum distillation, steam distillation or otherwise to isolate the desired oily material.

In order to remove the condensing agent prior to distillation it has been proposed to treat the upper layer with dilute acid or with a dilute alkali such as caustic soda, but such treatment has the disadvantage that frequently intractable emulsions are produced which are troublesome to work up, particularly when using dilute alkali, and in other cases even when the emulsions are not formed during this step, they frequently result if steam distillation is subsequently employed to remove the diluent or uncondensed hydrocarbon, as the case may be. The final product produced in this way is also frequently highly coloured.

We have now found that after treating the upper layer with a solid alkaline reacting material, such as slaked lime or sodium carbonate, or with an aqueous solution of ammonia or an alkaline reacting ammonium salt, the solvent or diluent can be removed by steam distillation under ordinary or reduced pressure without the formation of intractable emulsions. This method presents the further advantage that the final product is much lighter in colour than those normally prepared by the usual methods.

When the pretreatment is to be effected by using sodium carbonate or slaked lime, the upper layer may be merely shaken up with a small quantity of the reagent, and filtered; it can then be subjected directly to steam distillation to recover the inert diluent or excess of the aromatic hydrocarbon as the case may be. Alternatively the treatment may be effected by filtering the solution through a bed of the reagent preferably slightly moistened beforehand.

We prefer, however, to carry out the pretreatment of the solution using a concentrated solution of ammonia and this may be done by shaking together about .01 to .03 parts by weight of aqueous ammonia specific gravity 0.885 with each part of the solution. If the mixture is then allowed to stand it readily separates into an aqueous and a non-aqueous layer, the former of which can be removed, and the latter steam distilled after filtering through a bed of sand or otherwise to remove aluminium hydroxide which is precipitated by the treatment.

It is a further advantage of our invention that as there is no fear of emulsification of the oily solution during steam distillation it is possible to effect this latter step in a continuous manner, e.g. by passing the pretreated solution down a packed tower in countercurrent to an ascending stream of live steam. The inert diluent or its equivalent is then withdrawn from the top of the tower as vapour which may be condensed, dried and used again, while the oily material is withdrawn from the base of the tower together with condensed steam. As a result of the pretreatment to which the original solution has been subjected in accordance with our invention, an oily material readily resolves itself into a homogeneous

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layer and can be separated from the condensed steam. In many cases however, the oily product is extremely viscous, and in such circumstances it is desirable to accelerate the separation process by maintaining the liquid withdrawn from the base of the tower in a heated condition until resolution into two layers in complete.

However, our invention is not limited to cases where steam distillation is effected in a continuous manner, but can be usefully applied to batch processes also, and may be effected at ordinary or reduced pressures.

The following example, in which all parts are by weight, illustrates our invention applied to the treatment of the product obtained by reacting chlorinated paraffin wax with an excess of benzene in the presence of aluminium chloride, but it is to be understood that our invention is not limited to such a process, but is applicable to the treatment of any solution obtained by a process of the type hereinbefore referred to which involves the use of a volatile diluent which can be removed by steam distillation after the condensation is complete.

EXAMPLE.

650 parts of chlorinated paraffin wax containing 22.0% chlorine were reacted with 1060 parts of benzene in the presence of 45 parts of aluminium chloride. When reaction was complete and the mixture had been allowed to separate into two layers, the upper layer (1400 parts) was separated off, shaken with 25 parts of aqueous ammonia (specific gravity 0.885), and the oily layer filtered through sand. The filtered layer was then passed down a lagged column 4 feet high and packed with glass rings at the rate of 5 gms./min. while steam was introduced near the base at the rate of 10 gms./min. The vapours from the top were condensed, and the benzene separated while the mixture of lubricating oil and water from the base of the tower was kept at 60—70° C. for about 6 hours when the oil had separated out completely from the water. The latter was withdrawn leaving the oil as a transparent lemon-yellow material, which was dried by filtration through soda ash.

Dated the 11th day of November, 1936.

E. A. BINGEN,
Solicitor for the Applicants.

COMPLETE SPECIFICATION

Improvements in or relating to the Manufacture of Lubricating Oils

We, ARTHUR PEVERALL LOWES, of 154, Liverpool Road, Widnes, Lancashire, and DOUGLAS ELWOOD WHITE, of 24, Beaconsfield Crescent, Widnes, Lancashire, both British Subjects, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements in the manufacture of synthetic lubricating oils.

It is well known that oily materials suitable e.g. as lubricants, or as pour point depressants for lubricating oils, can be prepared by condensing chlorinated hydrocarbons of high molecular weight (i.e. of mean molecular weight above about 200) with aromatic hydrocarbons such as benzene or toluene, in the presence of a condensing agent such as aluminium chloride. Such condensations are frequently effected in the presence of an excess of the benzene or other aromatic hydrocarbon or of non-reacting diluents such as kerosene or benzine. The products separate usually into two layers, the upper one of which comprising the greater part of the oily material, together with the diluent and a very small fraction of the condensing agent, can be worked up by vacuum distillation, steam distillation or otherwise to isolate the desired oily material.

It has been proposed to modify the action of the catalyst by having present during the condensation metal salts, e.g. sodium chloride, copper chloride or zinc oxide. The use of ammonia has also been suggested.

In order to remove the condensing agent prior to distillation it has been proposed to treat the upper layer with dilute acid or with a dilute solution of an alkali such as caustic soda but such treatment has the disadvantage that intractable emulsions may be produced which are troublesome to work up, particularly when using dilute alkali. In other cases even when emulsions are not formed during this step, they frequently result if steam distillation is subsequently employed to remove the diluent or uncondensed hydrocarbon, as the case may be. Very often the final product made by these methods is highly coloured.

In specification No. 473,334, which though not published at the date of the present application bears a date prior thereto, there is claimed a process for the purification of crude products obtained by condensing halogenated aliphatic hydrocarbons with aromatic hydrocarbons in the presence of aluminium or anhydrous aluminium halide catalysts which comprises treating the crude product at an elevated temperature with ammonia or, at a temperature substantially not lower than 200° C. with a substantially anhydrous halide, sulphate or phosphate of a metal of Group I (including ammonium) or Group II of the periodic system or with an oxide or hydroxide of a metal of Group II or with mixtures thereof and thereafter separating the solid compound so formed. We make no claim herein to anything claimed in the said specification.

It is an object of our invention to provide a process whereby the condensing agent present in the upper layer from such condensations may be removed without the formation of emulsions. It is a further object of our invention to provide a method of removing the condensing agent in a manner which enables the diluent or uncondensed hydrocarbon to be removed subsequently, e.g. by steam distillation, without the formation of emulsions of the lubricating oil. A further object of the invention is to provide a method of making lubricating oils which are lighter in colour than oily products hitherto prepared by similar condensations.

According to the present invention, the upper layer of the reaction mixture obtained by condensing a chlorinated aliphatic hydrocarbon of high molecular weight (i.e. of mean molecular weight above about 200) with an aromatic hydrocarbon such as benzene or toluene in the presence of a condensing agent such as anhydrous aluminium chloride, is freed from condensing agent contained therein by treating it after separating it from the lower layer, with a solid alkaline reacting material, or with an aqueous solution of ammonia or of an alkaline reacting ammonium salt at ordinary or at slightly elevated temperatures, e.g. up to 30°—40° C. The manufacture of the lubricating oil from the material which has been so treated is then completed in the usual way, and in particular any unreacted aromatic hydrocarbon or inert diluent which may have been present during the condensation may be removed by steam distillation under ordinary or reduced pressure.

The treatment can be carried out satisfactorily at ordinary temperatures though if desired temperatures somewhat above this, e.g. up to 30°—40° C. may be used.

Examples of the solid alkaline reacting materials which may be used are slaked lime, anhydrous or hydrated sodium carbonate, sodium acetate, ammonium carbonate, sodium bicarbonate, zinc oxide and magnesium oxide. An example of a solution of an alkaline reacting ammonium salt which may be used is a solution of ammonium carbonate. The amount of the material which is used should not be less than that required to neutralize any free acid present in the reaction mixture and to decompose the condensing agent present, but apart from this we do not find that the amount of the alkaline material to be used is critical, or even that particular proportions give specially valuable results.

When the treatment according to our invention is to be effected by using a solid alkaline reacting material, e.g. slaked lime or sodium carbonate, the upper layer may be merely agitated, and thus thoroughly mixed, with a small quantity of the reagent and filtered. Alternatively the treatment may be effected by filtering the liquid through a bed of the reagent preferably slightly moistened beforehand. The condensing agent is completely removed by such simple treatments, and the filtered material can be worked up immediately; for example, it can be subjected directly to steam distillation to remove any inert diluent, or any excess aromatic hydrocarbon.

We prefer, however, to carry out the treatment of the upper layer using a concentrated solution of ammonia, and this may be done by thoroughly mixing it with about 1% to 3% of its weight of aqueous ammonia (specific gravity 0.885). If this mixture is then allowed to stand it readily separates into an aqueous and a non-aqueous layer, the former of which can be removed, and the latter steam distilled after filtering, e.g. through a bed of sand, to remove solid material which may be formed by the treatment. Thus, in the case where the condensing agent is aluminium chloride, aluminium hydroxide will be precipitated on treatment with ammonia solution, and will be removed by filtration. More dilute solutions of ammonia may also be used in this variation of our process, e.g. a solution of specific gravity 0.95, though we prefer to use more concentrated solutions.

It is a further advantage of our invention that as there is no fear of emulsification of the oily solution when it is steam distilled it is possible to carry out steam distillation of the material in a continuous manner, e.g. by passing the pretreated solution down a packed tower in countercurrent to an ascending stream of live steam. Any diluent or excess hydrocarbon is then withdrawn from the top of the tower as vapour which may be condensed, dried and used again, while the oil, free from diluent or excess aromatic hydrocarbon is withdrawn from the base of the tower together with condensed steam. As a result of the pretreatment to which the original material has been subjected in accordance with our invention, this mixture usually resolves itself into homogeneous layers of oil and water, which can be separated by decantation. In many cases, however, the product is extremely viscous, and in such circumstances it is desirable to accelerate the separation process by maintaining the liquid withdrawn from the base of the tower in a heated condition until resolution into two layers is complete.

However, our invention is not limited to cases where steam distillation is effected in a continuous manner, but can be applied usefully to batch processes also, and may be effected at ordinary or reduced pressures. It may also be applied where other methods of working up the material are used, e.g. where excess aromatic hydrocarbon or inert diluent present is removed by distillation *in vacuo*.

The following examples in which all parts are by weight, illustrate our invention as applied to the upper layer of the mixture obtained by reacting chlorinated paraffin wax with excess benzene in the presence of aluminium chloride, but it is to be understood that our invention is not limited to such a process, but is applicable to the treatment of the upper layer product from any similar condensation, where a small amount of the condensing agent has to be removed.

Example 1.

650 parts of chlorinated paraffin wax containing 22.0% chlorine were reacted with 1060 parts of benzene in the presence of 45 parts of aluminium chloride. When reaction was complete and the mixture had been allowed to separate into two layers, the upper layer (1400 parts) was separated off, agitated with 25 parts of aqueous ammonia (specific gravity 0.885) and filtered through sand. The filtrate was then passed at the rate of 5 gms./min. down a lagged column 1" in diameter and 4 feet high, packed with glass rings while steam was introduced near the base at the rate of 10 gms./min. The vapours from the top were condensed and the benzene separated, while the mixture of lubricating oil and water from the base of the tower was kept at 60—70° for about 6 hours when the oil had separated out completely from the water. The latter was withdrawn leaving a transparent lemon yellow oil which was dried by filtration through soda ash.

Example 2.

650 parts of chlorinated paraffin wax containing 25.4% chlorine were reacted with 1055 parts of benzene in the presence of 70 parts of anhydrous aluminium chloride. When the reaction was complete and the mixture had been allowed to separate into two layers, the upper layer weighing 1280 parts was separated off and filtered through a bed of sodium carbonate monohydrate in the form of small crystals. The clear, light coloured liquid was steam distilled to remove excess benzene and then maintained at 50° C. for a short time when the oil easily separated out from the condensed steam. Yield of oil 460 parts.

Example 3.

650 parts of chlorinated paraffin wax containing 29% chlorine were reacted with 1060 parts of benzene in the presence of 100 parts of anhydrous aluminium chloride. When reaction was complete and the mixture had separated into two layers the upper layer, weighing 1000 parts, was filtered through a bed of slaked lime and steam distilled as in Example 2. 420 parts of a light yellow oil were easily separated from the condensed steam.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the manufacture of condensation products by condensing a chlorinated aliphatic hydrocarbon of high molecular weight as hereinbefore defined with an aromatic hydrocarbon such as benzene or toluene in the presence of a condensing agent such as anhydrous aluminium chloride, which includes the step of separating the upper layer resulting from the condensation and treating the said layer at ordinary temperatures or at slightly elevated temperatures, e.g. up to 30°—40° C. with a solid alkaline reacting material or with an aqueous solution of ammonia or of an alkaline reacting ammonium salt.

2. Process as claimed in Claim 1 in which the treatment is effected by filtering the separated upper layer through a bed of the solid reagent.

3. Process as claimed in Claim 1 in which the separated upper layer is treated with 1—3% of its weight of a concentrated solution of ammonia, whereupon the non-aqueous layer is separated from the aqueous layer, filtered and steam

distilled.

4. Process as claimed in Claim 3 in which the steam distillation is carried out continuously by passing the material down a packed tower in countercurrent to live steam.

5. Process for the manufacture of condensation products suitable for use as lubricants substantially as hereinbefore described.

6. Condensation products of chlorinated hydrocarbons of high molecular weight with aromatic hydrocarbons whenever prepared by the methods claimed in any of the preceding claims.

Dated this 11th day of November, 1937.

E. A. BINGEN,
Solicitor for the Applicants.

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