PATENT SPECIFICATION

Application Date: April 12, 1937. No. 10413/37. **493,715**

Complete Specification Left: April 12, 1938.

Complete Specification Accepted: Oct. 12, 1938.

PROVISIONAL SPECIFICATION

Improvements in or relating to Manufacture of Oily Condensation Products

We, ARTHUR PEVERALL LOWES, of 154, Liverpool Road, Widnes, Lancashire, a British Subject, 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 oily materials.

It is well known that synthetic lubricating oils, pour point depressants, colouring matters for lubricants and the like, can be prepared by condensing long chain chlorinated aliphatic hydrocarbons with aromatic hydrocarbons in the presence of a catalyst of the Friedel-Craft type, such as aluminium chloride.

Normally, in such reactions the crude product separates into two layers, the upper one comprising the lubricating oil, together with excess of the aromatic hydrocarbon or the inert solvent (where such are present during the reaction) and a small amount of the catalyst, while the lower layer contains most of the catalyst associated with a liquid or resinous material which is valuable as an agent for imparting colour and fluorescence to lubricants. Various methods have been proposed for working up the reaction product to free it from the catalyst, such, for example, as treatment with water or acid or alkali. These methods frequently lead to the formation of water-oil emulsions which are difficult to break up. In copending Applications Nos. 10190/36 and 33351/36 there are described methods, free from these difficulties, in which the reaction product is heated with ammonium chloride or halides of the metals of groups I or II of the Periodic Table, whereupon the catalyst and the added salt form a granular solid which can readily be separated from the organic components by filtration or decantation.

We have now found that similar results can be obtained by adding to the reaction product a sulphate, phosphate or hydroxide of iron, chromium or aluminium, and heating to a suitable temperature, e.g. between 250—300° C. A granular solid is thereby formed consisting of the inorganic constituents of the mixture which is easily separated from the oily organic matter by filtration or decantation.

If desired, the whole of the crude reaction product may be treated with the metallic derivative, when a coloured fluorescent oil will be obtained as the ultimate product. Alternatively, the two layers of the crude product may be separated before working up, when the upper layer of the crude reaction product yields a light coloured lubricating oil while the lower layer yields a resinous or highly viscous material having a deep colour and an intense fluorescence.

A suitable amount of salt or hydroxide to add is between 1 and 2 mols. per mol. of catalyst present in the crude product or the part thereof which is being treated by the method of the invention, though smaller amounts, e.g. ½ mol, can be used if desired. Normally, heating for about half an hour suffices to bring about the separation of the catalyst, though longer heating periods can be used without any effect on the product beyond a slight reduction in the viscosity of the final product.

The invention may be further described with reference to the treatment of the crude product obtained by condensing chlorinated paraffin wax with an excess of benzene in the presence of aluminium chloride. At the completion of the condensation the finely divided salt, e.g. anhydrous ferrous sulphate, is added to the reaction mixture and the latter heated to about 280° C. for half an hour, during which period most of the excess benzene distils off. At the end of this period the aluminium chloride and the ferrous sulphate will have formed a granular solid which can be filtered off either directly or after cooling, when the deeply coloured fluorescent oil is obtained without further treatment.

The following examples further illustrate but do not limit our invention, all

parts being by weight:—

EXAMPLE 1.

650 parts of chlorinated paraffin wax containing 22% chlorine were treated with 1050 parts of benzene in the presence of 50 parts of anhydrous aluminium chloride, and the whole heated for 3 hours to 75° C. when evolution of hydrochloric acid had ceased. On cooling, the reaction mass formed two layers which were separated. 200 parts of the lower layer were heated with 40 parts of anhydrous ferrous sulphate for ½ hour at 300° C when the benzene distilled off, some hydrochloric acid gas was driven off, and the anhydrous aluminium chloride and ferrous sulphate formed a granular solid After cooling, the latter was removed by filtration when a red-green fluorescent oil was obtained of viscosity 200 centistokes at 100° F.

EXAMPLE 2.

200 parts of a lower layer obtained as in Example 1, were heated with 40 parts of aluminium hydroxide as described in that Example. An oil was obtained which had a viscosity of about 350 centistokes at 100° F. It was highly transparent, and had a yellow colour by transmitted light with a slight green fluorescence by reflected light.

Dated the 12th day of April, 1937.

E. C. G. CLARKE,
Solicitor for the Applicants.

COMPLETE SPECIFICATION

Improvements in or relating to the Manufacture of Oily Condensation Products

We, ARTHUR PEVERALL LOWES, of 154, Liverpool Road, Widnes, Lancashire, a British Subject, 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 oily condensation products.

It is well known that synthetic lubricating oils, pour point depressants, colouring matters for lubricants and the like, can be prepared by reacting long chain chlorinated aliphatic hydrocarbons with aromatic hydrocarbons in the presence of a condensing agent of the Friedel-Crafts type, such as aluminium chloride.

Normally, in such reactions the crude product separates into two layers, the upper one comprising the lubricating oil, together with excess of the aromatic hydrocarbon or the inert solvent (where such are present during the reaction) and a small amount of the condensing agent, while the lower layer contains most of the condensing agent associated with a liquid or resinous material which is valuable as an agent for imparting colour and fluorescence to lubricants. Various methods have been proposed for working up the reaction product to free it from the condensing agent, such, for example, as treatment with water or acid or alkali. These methods frequently lead to the formation of water-oil emulsions which are difficult to break up. In Specification 473,334 there are described methods free from these difficulties, in which the reaction product is heated with certain salts of a metal of Groups I or II of the Periodic Table, whereupon the catalyst and the added salt form a granular solid which can readily be separated from the organic components by filtration or decantation.

According to the present invention, crude reaction products obtained by condensing chlorinated aliphatic hydrocarbons of high molecular weight as hereinafter defined, with aromatic hydrocarbons such as benzene or toluene in the presence of aluminium or anhydrous aluminium chloride, are mixed with an hydroxide or an anhydrous sulphate or phosphate of iron, chromium, or aluminium, heated to above 200° C. and preferably to between 250 and 300° C. and the oily constituents separated, e.g. by decantation or filtration.

By treating the crude product in this way the inorganic constituents are converted to a granular mass, and the subsequent separation from the oily matter is effected readily and efficiently.

By an aliphatic hydrocarbon of high molecular weight we mean one with a molecular weight above 200, or in the case of a technical mixture of hydrocarbons a mean molecular weight above this figure. Typical hydrocarbons which may be used include the gas oils, paraffin wax, and wax sweatings. The chlorine content of the chlorinated aliphatic hydrocarbons taking part in the condensation is not critical. Thus chlorinated paraffin waxes containing 20% or 40% chlorine are eminently suitable.

If desired, the whole of the crude reaction product may be treated with the metallic derivative, when a coloured fluorescent oil will be obtained as the ultimate product. Alternatively, the two layers of the crude product may be separated before working up, when the upper layer of the crude reaction product yields a light coloured lubricating oil while the lower layer yields a material which is usually of an oily nature but may be almost resinous and possesses a deep colour and an intense fluorescence.

A suitable amount of inorganic salt or hydroxide to add is between 1 and 2 mols. per mol. of the condensing agent present in the crude product, or the part thereof which is being treated by the method of the invention, though smaller amounts, e.g. ½ mol. can be used if desired. Normally, heating for about half an hour suffices to bring about the separation of the condensing agent, though longer heating periods can be used without any effect on the product beyond a slight reduction in the yield and viscosity of the final product. Greater quantities than this can also be used though we find that no advantage accrues from doing so; on the other hand, filtration or decantation will not be as effective in separating the organic constituents because of the relatively large amount entrained in the granular solid, though this may be overcome by extracting the organic constituent with benzene or other solvent which can be subsequently removed by evaporation.

The invention will be further described with reference to the treatment of the crude product obtained by condensing chlorinated paraffin wax with an excess of benzene in the presence of aluminium chloride. At the completion of the condensation the finely divided salt e.g. anhydrous ferrous sulphate, is added to the reaction mixture and the latter heated to about 280° C. for half an hour until most of the excess benzene has distilled off. At the end of this period the aluminium chloride and the ferrous sulphate will have formed a granular solid which can be filtered off either directly or after cooling, when the deeply coloured fluorescent oil is obtained without further treatment.

The following examples further illustrate but do not limit our invention, all parts being by weight:—

EXAMPLE I.

650 parts of chlorinated paraffin wax containing 22% chlorine were treated with 1050 parts of benzene in the presence of 50 parts of anhydrous aluminium chloride, and the whole heated for 3 hours to 75° C. when evolution of hydrochloric acid had ceased. On cooling, the reaction mass formed two layers which were separated. 200 parts of the lower layer were heated with 40 parts of anhydrous ferrous sulphate for ½ hour at 300° C. when the benzene distilled off, some hydrochloric acid gas was driven off, and the anhydrous aluminium chloride and ferrous sulphate formed a granular solid. After cooling, the latter was removed by filtration when a red-green fluorescent oil was obtained of viscosity 200 centistokes at 100° F.

EXAMPLE II.

200 parts of a lower layer obtained as in Example 1, were heated with 40 parts of aluminium hydroxide as described in that Example. An oil was obtained which had a viscosity of about 350 centistokes at 100° F. It was highly transparent and had a yellow colour by transmitted light with a slight green fluorescence by reflected light.

EXAMPLE III.

650 parts of a chlorinated paraffin wax containing 25% chlorine were condensed with 600 parts of benzene in the presence of 50 parts anhydrous aluminium chloride, the reaction being carried to completion by heating to 75° C. for 3 hours while stirring vigorously. 300 parts of the crude product were mixed with 30 parts of chromium hydroxide and the mixture heated over a period of 2 hours to 280° C. Excess benzene distilled off, some hydrogen chloride was evolved and the inorganic constituents of the mass were converted to a black granular solid which settled from the oil. After cooling the supernatant liquid was filtered to remove any solid remaining in suspension, and a clear oil was obtained having a red-green fluorescent appearance and a viscosity of 205 centistokes at 100° F.

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 oily condensation products from the crude reaction products obtained by condensing chlorinated aliphatic hydrocarbons of high molecular weight with aromatic hydrocarbons in the presence of aluminium or anhydrous aluminium chloride which comprises treating the said crude reaction products with an hydroxide or an anhydrous sulphate or phosphate of iron, chromium or aluminium, heating to above 200° C., and preferably to between 250° and 300° C., and separating the oily constituents, e.g. by decantation or filtration.

2. Process as claimed in Claim 1 in

which the crude reaction product is first allowed to separate into two layers and thereafter one or both of the layers are separately subjected to the treatment as aforesaid.

3. Process as claimed in Claims 1 or 2 in which the amount of inorganic salt or hydroxide added is from 1 to 2 mols. per mol. of the condensing agent in the product or part thereof undergoing treatment.

4. Process for the manufacture of oily condensation products substantially as hereinbefore described and illustrated with reference to the foregoing Examples.

5. Oily condensation products whenever prepared by the methods claimed in any of the preceding claims.

Dated the 12th day of April, 1938.

E. C. G. CLARKE,
Solicitor for the Applicants.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1938.