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COMPLETE SPECIFICATION

The Separation of Oxygen-containing Compounds derived from Hydrocarbons

We, N.V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ of 30, Carel van Bylandtlaan, The Hague, The Netherlands, a Netherlands 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 a process for separating mixtures of various oxygen-containing compounds derived from hydrocarbons and which are insoluble or practically insoluble in water. In the following description and in the claims hereinafter appearing the expression "water-insoluble oxygen-containing compounds" means oxygen-containing compounds derived from hydrocarbons which compounds are insoluble or practically insoluble in water.

It has already been proposed in Specification No. 527080 to separate a mixture of polar organic isomeric compounds, wherein the isomerism is due to a difference in the position of one or more polar groups in the molecule, by extraction with the aid of two solvents, preferably moving in counter-current, which have such a difference in polarity that under the conditions of the extraction two liquid phases are formed. The present invention is not concerned with the separation of mixtures of isomeric compounds of the aforesaid type and the references to mixtures of water-insoluble oxygen-containing compounds in this specification and in the claims hereinafter appearing are to be construed accordingly.

Mixtures of water-insoluble oxygen-containing compounds are formed, for example, as by-products in the manufacture of synthetic hydrocarbons, as in the Fischer-Tropsch process, in which carbon monoxide and hydrogen are used as initial materials. In these syntheses oxygen-containing compounds of a more or less pronounced polar character, such as acids, esters, ketones, aldehydes, alcohols and ethers, are formed as by-products in addition to the desired hydrocarbons. The compounds of a more pronounced polar character generally result from a higher degree of oxidation than the less polar ones. In so far as these oxygen-containing compounds are soluble in water they are very easily extractable by means of water and can be separated by such means from the other reaction products which consist of a mixture of hydrocarbons and higher oxygen-containing compounds which are insoluble or practically insoluble in water. By extraction with a selective solvent these water-insoluble oxygen-containing compounds can be separated from the hydrocarbons.

Mixtures of water-insoluble oxygen-containing compounds are also formed in the Oxo process, in which, starting from carbon monoxide and olefines, oxygen-containing compounds are prepared synthetically.

The mixtures of products obtained in the preparation of synthetic hydrocarbons do not, as a rule, contain more than approximately two per cent of water-insoluble oxygen-containing compounds. If, however, a suitable method were available for separating these compounds from each other, it would be worth while commercially to increase this percentage to 10 per cent or more by modifying the catalyst and reaction conditions.

The present invention aims at providing a simple and cheap method of separating mixtures of water-insoluble oxygen-containing compounds into fractions, one of which contains compounds of a more pronounced and the other compounds of a less pronounced polar character. Such a process is important, since these oxygen compounds represent very valuable products and the mixtures referred to above have hitherto been considered worthless as a source thereof on account of the difficulties attached to their separation.

According to this invention a mixture of water-insoluble oxygen-containing compounds is separated into a fraction containing compounds of a more pronounced polar character and a fraction containing compounds of a less pronounced polar character by subjecting such mixture to the action of two solvents passed in counter-current to

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each other, the one solvent consisting wholly or partially of substances the molecules of which either contain two or more polar groups or consist of one polar group and a highly polarizable remainder, the other solvent consisting entirely or substantially of one or more paraffinic hydrocarbons with a boiling range outside the boiling limits of the mixture to be separated.

The extraction process of this invention is preferably applied to mixtures with a relatively narrow boiling range, for example, where the initial and final boiling points are from 10 to 40° C. apart. Such mixtures cannot be separated into a fraction containing compounds of a more pronounced polar character and a fraction containing compounds of a less pronounced polar character by ordinary distillation.

The distribution among the solvents of the compounds to be separated is not only dependent on their polarities and chemical properties, but also on the sizes of the molecules, and this accounts for the fact that when starting from fractions with long boiling ranges the separation will generally be incomplete.

When starting, for example, with a mixture of alcohols and ketones with a long boiling range, the conditions under which the extraction takes place can be selected in such a way that in one phase only the alcohols with a low molecular weight are taken up, while all the ketones and the remainder of the alcohols are found in the other phase. The conditions can also be selected in such a way that in one phase only some of the ketones, namely those with high molecular weights, are taken up and in the other phase the remainder of the ketones and all the alcohols are collected. It will be clear from the above that, between these two extremes, all kinds of intermediate distributions can be brought about. Generally it will not be possible, therefore, to effect a complete separation between alcohols and ketones.

Consequently, if it is desired to separate mixtures with long boiling ranges by the present extraction process it is preferable first to separate these mixtures into narrow fractions by ordinary distillation.

Since the oxygen-containing compounds to be separated are insoluble or practically insoluble in water, the mixtures of these compounds will mainly comprise substances with more than five carbon atoms and will usually have an initial boiling point higher than approximately 110° C. The best results are obtained with mixtures with boiling points not higher than approximately 250° C.

Hydroxy compounds, with or without ether groups are preferably used as polar solvents. Excellent results can be obtained with glycols or glycol ethers, more particularly with diethylene glycol. Examples of solvents with two or more polar groups are the poly-alcohols, butylene glycols, hexylene glycols, poly-alcohol ethers, poly-ethylene glycols, phenyl ethers of glycol, glycerine dimethyl ether, alkanol amines, oxy-nitro compounds, such as orthonitrophenol, and the chlorohydrins.

Examples of solvents with a single polar group, the remainder of the molecule being highly polarizable, are: nitrobenzene, phenol, cresols, furfural, phenyl glycid ether, sulpholenes and substituted sulpholenes. Very suitable results are also obtained with sulpholane or substituted sulpholanes.

The boiling range of the polar solvent need not be outside that of the mixture to be separated. If the boiling ranges overlap wholly or partially the solvent can be recovered by extraction with water, since the polar solvent is usually water-soluble, whereas the compounds to be separated are insoluble or practically insoluble in water.

If the boiling ranges of the solvent and the mixture to be separated do not overlap and the solvent is recovered by distillation (which will generally be the case), solvents with boiling points higher than those of the compounds to be separated are preferred. The extraction according to the invention is, as a rule, carried out with an excess of solvents, so that when using a solvent with a high boiling point only the relatively small quantity of oxygen-containing compounds need be distilled off.

The second solvent may consist of pure paraffinic hydrocarbons or of petroleum fractions containing no or practically no aromatics, for example benzine fractions poor in aromatics. Paraffinic hydrocarbons are insoluble in water and consequently cannot be separated from the water-insoluble, oxygen-containing compounds by extraction with water. The recovery of the second solvent must therefore be effected by distillation, so that the boiling range of this solvent must be outside, i.e. either above or below, that of the mixture to be separated.

Since, as a rule, the second solvent is also used in excess, it is preferred to use a hydrocarbon fraction poor in or free from aromatics, the boiling range of which is higher than that of the mixture to be separated, such as liquid paraffin.

The extraction is, as a rule, carried out at temperatures of from 0 to 100° C. In some cases the efficiency of the extraction process of this invention can be greatly improved by maintaining a temperature gradient over the whole or part of the extraction zone. Preferably a gradual fall of temperature is employed.

The solvents must of course be selected

in such a way that two liquid phases are formed in order that countercurrent flow may be effected. The more polar the character of the polar solvent the smaller is its dissolving power for the oxygen-containing compounds, which should be borne in mind when selecting this solvent. It may sometimes be preferable to use a mixture of polar solvents. Moreover there may be added to the polar solvent a substance which more or less modifies the character of the solvent, for example its dissolving power or selectivity. Such a substance may be for example, water. By adding water the total dissolving power of the solvent decreases, which causes the selectivity of the solvent mixture to increase.

The invention will be further illustrated with reference to the following examples.

EXAMPLE I

A mixture of 50 vol.% n-butanol-1 (boiling point 118° C.) and 50 vol.% methyl isobutyl ketone (boiling point 116° C.) was used as initial material. This mixture was fed to the middle stage of a 7-stage extraction column. For each part by volume of this mixture flowing through the column 1.6 parts by volume of diethylene glycol were fed into the first stage and 6.4 parts by volume of liquid paraffin were fed into the seventh stage. These solvents were passed through the column in countercurrent flow.

The material recovered from the diethylene glycol phase contained 98.5% of butanol and only 1.5% of methyl isobutyl ketone. The material recovered from the liquid paraffin phase contained 98.5% of ketone and 1.5% of butanol.

EXAMPLE II

A mixture of 50 vol.% 2-methylhexanol-1 (boiling point 167° C.) and 50 vol.% diisobutyl ketone (boiling point 169° C.) was used as initial material. This mixture was fed to the middle stage of an 11-stage extraction apparatus. For each 2 parts by volume of this mixture flowing through the apparatus 11.3 parts by volume of diethylene glycol were fed into the first stage and 8.7 parts by volume of liquid paraffin were fed into the eleventh stage. These solvents were passed through the apparatus in countercurrent flow. The material recovered from the diethylene-glycol phase contained 98.7% of 2-methylhexanol-1 and 1.3% of diisobutyl ketone. The material recovered from the liquid paraffin phase contained 98.7% of the ketone and 1.3% of 2-methylhexanol-1.

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. A process for separating a mixture of water-insoluble oxygen-containing compounds into a fraction containing compounds with a more pronounced polar character and a fraction containing compounds with a less pronounced polar character wherein the mixture is subjected to the action of two solvents flowing in countercurrent to each other, one solvent consisting entirely or substantially of substances the molecules of which either contain two or more polar groups or consist of one polar group and a highly polarizable remainder, and the other solvent consisting entirely or substantially of one or more paraffinic hydrocarbons with a boiling range outside the boiling limits of the mixture to be separated.

2. A process as claimed in claim 1, wherein the mixture to be separated boils at a temperature between approximately 110° C. and 250° C.

3. A process as claimed in claim 1 or 2 wherein the mixture to be separated has initial and final boiling points not more than 40° C. apart.

4. A process as claimed in claim 1, 2 or 3 wherein the first-named solvent is an organic hydroxy compound.

5. A process as claimed in claim 4, wherein the said organic hydroxy compound is a glycol.

6. A process as claimed in claim 4, wherein the said organic hydroxy compound contains one or more ether groups.

7. A process as claimed in claim 6 wherein the said organic hydroxy compound is a glycol ether.

8. A process as claimed in claim 6, wherein the said organic hydroxy compound is diethylene glycol.

9. A process as claimed in claim 1, 2 or 3 wherein the first-named solvent is sulpholane or a substituted sulpholane.

10. A process as claimed in any one of the preceding claims, wherein the second solvent consists of high-boiling paraffinic hydrocarbons, such as liquid paraffin.

11. A process as claimed in any of the preceding claims wherein the mixture to be separated has been derived from the products of a Fischer-Tropsch or Oxo process.

12. A process for separating a mixture of water-insoluble oxygen-containing compounds substantially as hereinbefore described and with reference to the Examples.

13. Products separated from a mixture of water-insoluble oxygen-containing compounds by a process as claimed in any of the preceding claims when prepared or produced by the methods or processes of manufacture particularly described and ascertained.

Dated this 30th day of June 1949.

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