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2,847,356

FLOTATION DEWAXING

Willem Johan Pieters, Lucas Alders, and Johannis Doorn,
Amsterdam, Netherlands, assignors to Shell Development
Company, Emeryville, Calif., a corporation of
Delaware

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This invention relates to a process for the separation of solid wax from wax-containing oil, and particularly relates to a process for the separation of a mixture of solid wax and oil, e. g., of a paraffin wax concentrate, by means of flotation.

It is well-known to dewax oil containing solid wax by cooling the oil to a temperature at or slightly below the desired pour point of the oil product and separating the thus produced solid wax particles from the cooled oil-wax mixture by flotation with a gas which is passed through said mixture. The rising gas bubbles form a foam or froth on the surface of the oil, and the wax particles are entrained therein. The wax-containing foam is then separated from the essentially solid wax-free bulk of the oil by any known process, such as skimming. Among the many foam-producing gases which are suitable in this method are air, nitrogen, methane, ethane, propane, and the like. The gas can be introduced into the oil-wax mixture from an external source, or it may be formed in situ, as, for example, by lessening the external pressure on a mixture of the wax, oil and a liquefied gas, such as propane.

Although the flotation dewaxing technique has been known for many years and is an effective method of producing an oil substantially free of wax at the temperature of separation, practically no commercial application has been made of it, this primarily because a substantial amount of oil is entrained with the foam, which results in an uneconomically low yield of dewaxed oil as well as an undesirably high contamination of the wax product with oil.

A principal object of the present invention is to provide an improved and commercially practicable method for the flotation dewaxing of a wax-containing oil. A more specific object of the present invention is to improve the dewaxed oil yield in a process of flotation dewaxing. Another object is to make possible the recovery of a wax product containing a relatively smaller proportion of oil in a dewaxing process utilizing the wax flotation technique. Other objects of the invention will become apparent hereinafter.

It has now been discovered that the application or use of a small (minor) amount of a surface-active agent, which is at least partially oil soluble to the oil-wax mixture, will make possible the attainment of a much higher oil yield and a wax product of a much lower oil content, when these surface-active agents are used in the flotation dewaxing of oils.

The mechanism by which these advantages are accomplished is not entirely clear. In recent years much has been learned about the interrelationship of surface forces in multi-phase systems, but the determination of factors which change these forces is still ordinarily an empirical matter. With respect to the gas-oil-wax system encountered in flotation dewaxing, it is plausible that when no surface-active agent is present the solid wax particles attract each other and thereby have a tendency to clot,

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resulting in the enclosure of oil between the wax particles. When such particles are entrained by the gas bubbles, aggregates are formed which move with difficulty, do not easily disintegrate and therefore no longer release the enclosed oil. It is possible that, when surface-active agents are added to the oil-wax mixture the surface-active agent will adhere to the wax particles and cause them to repel each other, so that clotting takes place to a lesser extent or not at all, the wax laden bubbles move more easily through the oil, and there is less tendency for the oil to become enclosed in the wax. Another possible theory is that the surface-active agent will decrease the tendency of the oil to wet the wax particles (that is, will increase the three-phase contact angle between the wax-oil interface and the oil-gas interface, through the oil phase) so that the oil will drain from the wax particles more rapidly. It is, at any rate, certain that the explanation is not a simple one. For example, in U. S. Patents Nos. 2,645,597, 2,645,598, 2,645,599 and 2,645,600, there is set forth an experimentally proven explanation of processes of dewaxing wherein an aqueous solution of a surface-active agent is employed to promote the separation of oil-wax mixtures. In accordance with the teaching of these patents one would expect, as it is indeed expressly stated therein, that the aqueous phase is essential to the promotion of a separation of wax from an oil-wax mixture by flotation, and yet we have found that such is not the case. The essence of the present invention is the discovery that the addition of at least partially oil-soluble surface-active agents, in certain concentrations, directly to an oil-wax mixture will accomplish the desired results and purposes set out hereinabove and we therefore do not wish to be limited to any theoretical explanation.

In practicing the present invention, it is generally necessary to add only a small quantity of a surface-active agent to the oil-wax mixture. It has been found that good results are obtained when the concentration of the surface-active agent is as low as 0.01% by weight of the mixture. In some cases it can be as high as 1.0% by weight. It is preferred to use at least 0.05% by weight. Particularly good results are obtained when less than 0.7% by weight is added.

The surface-active agent used can be any of the conventional chemicals denoted by that name which are at least partially oil-soluble. For example, particularly good results were obtained by the addition of olefin polymers, such as "Paratone" (polyisobutene) and ethene oxide polymers, such as "Triton X-45" (a mixture of alkyl aryl polyethoxy alcohols). Other examples of the broad class of operable surface-active agents useful in the practice of the invention include alkyl or alkyl-aryl compounds substituted by one or more polar groups, in particular alkyl-aryl sulphonates and alkyl-aryl phosphates, such as calcium petroleum sulphonates, and alkyl salicylates, such as calcium alkyl salicylate. Silicones, such as Dow Corning "D. C. 4 Compound," and condensation products of chlorinated hydrocarbons and naphthalenes, such as "Paraflo," are also especially useful. The surface-active agents can be used singly or in mixtures and can be applied in a pure form or in an oil concentrate thereof. The surface-active agent can be used before and/or during the flotation process and can be added to the foam, to the oil, or as a mist in the entering gas.

The present invention can be applied in a flotation process in one or in several stages. If there is more than one stage, the first stage will be at an intermediately low temperature, and the separation of the foam from the oil is effected as in a one-stage process. Then, however, the wax-containing foam from the first stage is heated to a slightly higher temperature at which some,

but not all, of the wax is melted, and the flotation process repeated at this slightly higher temperature. The wax-free or nearly wax-free oil phase from the first stage is then cooled to a lower temperature and the flotation process repeated at this lower temperature. Similarly, more stages can be used. In such a multi-stage process the foam phase from each stage will be transferred to the stage of the next higher temperature and the oil phase from each stage will be transferred to the stage of the next lower temperature, thus increasing the sharpness of separation between the wax and the oil by means of a rectification effect. A surface-active agent can be applied advantageously in each of the stages. It will also be evident that the technique can be carried out in either a batch or a continuous process.

If the oil-wax mixture is too viscous for rapid separation of the wax, diluents can and should be added to it. For best results the viscosity of the mixture at the flotation temperature should not be higher than 50 centipoises and preferably no higher than 25 centipoises. Although non-polar solvents will usually be selected, it is occasionally of benefit to employ a relatively polar solvent.

As hereinabove stated, the process of the present invention does not require the presence of a separate aqueous phase. This improvement is highly advantageous and greatly enhances the commercial practicability of the flotation process because an oil product, containing no more water than does the charge stock, is obtained directly from the floatation step without the necessity of subsequent and additional separation and drying steps. However, some of the charge stocks for which the process is suitable can contain some dissolved or dispersed water in small quantities. Water in solution at the separation temperature is not harmful and it has been found that as long as any separate water phase present amounts to less than about 1.0% by weight, and preferably less than about 0.5% by weight, based on the weight of the original oil-wax mixture, the benefits of the invention are still realized.

A particularly effective method of practicing the invention is to use the same substance as both the flotation gas and the refrigerant to cool a waxy oil and precipitate the wax therein. Thus, liquefied propane, for example, is mixed with the waxy oil containing a surface-active agent and permitted to vaporize by a lessening of the external pressure on the system. The resulting formation of gaseous propane reduces the temperature of the oil and precipitates wax, and the rising gas bubbles produce a wax-bearing froth, which can then be separated to recover the wax and oil products. Instead of propane it is possible to use any substance which is capable of vaporizing at the desired dewaxing temperature. A large number of substances meet this requirement because the external pressure on the system can be adjusted at will to effect the vaporization of the substance over a broad range of temperatures. Other examples of particularly suitable substances for the purpose are carbon dioxide, ethylene and propylene. It will be evident to those skilled in the art that many other substances are also suitable. This particular application of the process may be varied extensively. For example, the surface-active agent can be mixed into the oil either before or after the vaporizing material has been introduced into the oil. Any of the common viscosity-reducing dewaxing solvents or diluents, either polar or non-polar, can be present. The process can be carried out in either a single stage or in several stages and it can be either batch or continuous.

The wax concentrate obtained by means of the present invention can be further treated by any of the conventional methods of pressing, sweating, or deoiling with solvents if a purer wax is desired.

The following examples are given for the purpose of

further elucidating the invention and to show especially effective applications of it, but are not to be considered limitations on its scope:

Example I

A gas oil containing 1.4% by weight of solid wax at 10° C. was separated at this temperature by the conventional flotation technique as follows: The oil-wax mixture was placed in a vertical tube the bottom of which contained a frittered glass filter. Nitrogen was blown through the filter into the oil-wax mixture. A foam layer was produced on the surface of the oil and was recovered by skimming. The remaining oil phase was essentially free of solid wax as evidenced by its pour point of 12° C. The oil phase yield was 75% by weight of the original mixture; therefore the recovered foam amounted to 25% by weight of the original mixture and contained an oil to wax ratio of

$$\frac{25-1.4}{1.4}$$

or 16.9.

Next, in accordance with the present invention, exactly the same procedure was followed except that 0.5% by weight of "Paraflow" (condensation product of chlorinated paraffin wax and naphthalene) was added to the original oil-wax mixture. The oil yield was thereby raised from 75% (by the conventional technique) to 85% by weight by the use of a surface-active agent in accordance with the present invention. The oil to wax ratio in the recovered foam phase was reduced from 16.9 to 9.7.

Example II

The conventional procedure of Example I was again repeated except that now 0.1% by weight of "Paratone" (polyisobutene) was added to the original oil-wax mixture. The oil yield was thereby increased to 86.3% by weight and the oil to wax ratio in the foam was reduced to 8.8.

Example III

The conventional procedure of Example I was again repeated except that now 0.2% by weight of a 50% by weight solution of calcium petroleum sulphonate in mineral oil was added to the original oil-wax mixture. The oil yield was thereby increased to 84.6% by weight and the oil to wax ratio in the foam was reduced to 10.

Example IV

The conventional procedure of Example I was again repeated except that now 0.2% by weight of a 50% by weight solution of calcium C₁₄₋₁₈-alkyl salicylate in mineral oil was added to the original oil-wax mixture. The oil yield was thereby increased to 78.0% by weight and the oil to wax ratio in the foam was reduced to 14.7.

Example V

The conventional procedure of Example I was again repeated except that now 0.1% by weight of "Triton X-45" (an alkyl aryl polyethoxy alcohol) was added to the original oil-wax mixture. The oil yield was thereby increased to 80.3% by weight and the oil to wax ratio in the foam was reduced to 13.0.

Example VI

The conventional procedure of Example I was again repeated except that the original oil-wax mixture was a distillate gas oil from a different crude oil. The oil yield was 70% by weight. The addition of 0.1% by weight of "D. C. 4 Silicone Compound" was added to a quantity of original oil-wax mixture and the procedure repeated. The oil yield was thereby increased to 86% by weight.

The present invention is applicable to all wax-bearing oils. The charge stock can be a distillate stock or a

residue. Mineral oils, brown coal tar oils, shale oils, vegetable and animal oils and synthetically produced oils, any of which may have been previously subjected to a deasphalting treatment or other treatment for the purpose of improving their physical and/or their chemical nature, are illustrative of sources of oils which can be advantageously dewaxed by the method of the present invention. The invention is applicable and advantageous in the manufacture of any of the usual products derived from the above-mentioned sources, including, for example, lubricating oils and greases, furnace and other heating oils (both industrial and domestic), internal combustion engine fuels such as diesel oils and jet fuels, waxy charge stocks for cracking processes, wax products for industrial, pharmaceutical and chemical intermediate use, and many others.

We claim as our invention:

1. In a flotation process of dewaxing oils wherein a mixture of solid wax and oil is separated into an oil product containing a smaller proportion of wax than in said mixture and a wax product containing a smaller proportion of oil than in said mixture by means of a passing of a gas through said mixture to a surface thereof in the presence of less than about 1% by weight of a separate aqueous phase thereby producing a wax-bearing gaseous froth and a remaining oil phase as the only liquid phase and separating said wax-bearing froth from said remaining oil phase, the improvement comprising effecting said passing of gas through said mixture in the presence of a minor amount of an at least partially oil-soluble surface-active agent.

2. In a flotation process of dewaxing oils wherein a mixture of solid wax and oil is separated into an oil product containing a smaller proportion of wax than in said mixture and a wax product containing a smaller proportion of oil than in said mixture by means of a passing of a gas through said mixture to a surface thereof in the presence of less than about 1% by weight of a separate aqueous phase thereby producing a wax-bearing gaseous froth and a remaining oil phase as the only liquid phase and separating said wax-bearing froth from said remaining oil phase, the improvement comprising effecting said passing of gas through said mixture in the presence of from about 0.01% to about 1.0% by weight of an at least partially oil-soluble condensation product of chlorinated hydrocarbon and naphthalenes.

3. In a flotation process of dewaxing oils wherein a mixture of solid wax and oil is separated into an oil product containing a smaller proportion of wax than in said mixture and a wax product containing a smaller proportion of oil than in said mixture by means of a passing of a gas through said mixture to a surface thereof in the presence of less than about 1% by weight of a separate aqueous phase thereby producing a wax-bearing gaseous froth and a remaining oil phase as the only liquid phase and separating said wax-bearing froth from said remaining oil phase, the improvement comprising effecting said passing of gas through said mixture in the presence of from about 0.01% to about 1.0% by weight of an olefin polymer.

4. In a flotation process of dewaxing oils wherein a mixture of solid wax and oil is separated into an oil product containing a smaller proportion of wax than in said mixture and a wax product containing a smaller proportion of oil than in said mixture by means of a passing of a gas through said mixture to a surface thereof in the presence of less than about 1% by weight of a separate aqueous phase thereby producing a wax-bearing gaseous froth and a remaining oil phase as the only liquid phase and separating said wax-bearing froth from said remaining oil phase, the improvement comprising effecting said passing of gas through said mixture in the

presence of from about 0.01% to about 1.0% by weight of an alkyl-aryl sulphonate.

5. In a flotation process of dewaxing oils wherein a mixture of solid wax and oil is separated into an oil product containing a smaller proportion of wax than in said mixture and a wax product containing a smaller proportion of oil than in said mixture by means of a passing of a gas through said mixture to a surface thereof in the presence of less than about 1% by weight of a separate aqueous phase thereby producing a wax-bearing gaseous froth and a remaining oil phase as the only liquid phase and separating said wax-bearing froth from said remaining oil phase, the improvement comprising effecting said passing of gas through said mixture in the presence of about 0.1% by weight of polyisobutene.

6. In a flotation process of dewaxing oils wherein a mixture of solid wax and oil is separated into an oil product containing a smaller proportion of wax than in said mixture and a wax product containing a smaller proportion of oil than in said mixture by means of a passing of a gas through said mixture to a surface thereof in the presence of less than about 1% by weight of a separate aqueous phase thereby producing a wax-bearing gaseous froth and a remaining oil phase as the only liquid phase and separating said wax-bearing froth from said remaining oil phase, the improvement comprising effecting said passing of gas through said mixture in the presence of about 0.2% by weight of a 50% by weight solution of calcium petroleum sulphonate in mineral oil.

7. In a flotation process of dewaxing oils wherein a mixture of solid wax and oil is separated into an oil product containing a smaller proportion of wax than in said mixture and a wax product containing a smaller proportion of oil than in said mixture by means of a passing of a gas through said mixture to a surface thereof in the presence of less than about 1% by weight of a separate aqueous phase thereby producing a wax-bearing gaseous froth and a remaining oil phase as the only liquid phase and separating said wax-bearing froth from said remaining oil phase, the improvement comprising effecting said passing of gas through said mixture in the presence of from about 0.05% to about 0.7% by weight of a silicone compound.

8. In a flotation process of dewaxing oils wherein a mixture of solid wax and oil is separated into an oil product containing a smaller proportion of wax than in said mixture and a wax product containing a smaller proportion of oil than in said mixture by means of passing of a gas through said mixture to a surface thereof in the presence of less than about 1% by weight of a separate aqueous phase thereby producing a wax-bearing gaseous froth and a remaining oil phase as the only liquid phase and separating said wax-bearing froth from said remaining oil phase, the improvement comprising effecting said passing of gas through said mixture in the presence of from about 0.01% to about 1.0% by weight of an at least partially oil-soluble condensation product of chlorinated paraffin wax and naphthalene.

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