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DEMULSIFICATION OF PETROLEUM

Abraham Shapiro, Monrovia, Calif., assignor to Socony-Vacuum Oil Company, Incorporated, New York, N. Y., a corporation of New York

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The invention relates to the resolution of petroleum emulsions and particularly to the demulsification of crude petroleums.

Secondarily the invention relates to materials for the rapid and accurate determination, by the solution method, of the total amount of water in crude petroleums containing emulsion.

It is well known that some petroleums in which part or all of the water is in the emulsified form are highly resistant to electrostatic resolution or to chemical demulsification as produced, for example, by the addition to the oil of soaps, fatty acid esters, etc.

I have discovered that in cases where the electrical treatment is slow or ineffective or in which addition to the oil of a normal dose of an ordinarily effective chemical demulsifying agent fails to produce prompt resolution, investigation will usually show that the water present in the oil is either very high or very low in pH value. For example, it is not uncommon to find the separated water showing a pH value as high as 9 to 11 or as low as 3.5 to 4, and in such cases the sedimentation of the water following electrostatic treatment or the addiiton of a treating agent is likely to be slow and imperfect.

I have also discovered that when the pH of the water is brought, by the addition to the emulsified oil of suitable acid or alkaline reagents, to approximately a value of 5.2, or at least within the range 5.5 to 4.8, both the rapidity and the completeness of separation and stratification are greatly increased.

In the commercial demulsification of large quantities of crude petroleum a sample of the water contained in the oil should first be separated and its pH value determined; also the percentage of water present should be ascertained. This being done, the quantity of the acid or alkaline substance required to bring the ascertained quantity of water to a pH approximating 5.2 is to be added to and blended with the oil.

In selecting the reagent used to change the pH of the water, it is important to provide for introducing the reagent into the water phase with the least possible agitation of the oil, as any undue agitation is likely to increase the quantity of emulsion or to tighten emulsions already present. For that reason a volatile acid or alkali, such as hydrochloric acid or ammonia is preferable to a nonvolatile reagent such as sulfuric acid or caustic soda, as the volatile reagents tend much more strongly to spontaneous dispersion through the mass and to equalization of pH value between the larger particles of free water in which the reagent first dissolves and the minute emulsified water particles. In many cases, however, nonvolatile reagents such as sulfuric, oxalic, or citric acid and sodium or potassium hydroxide or carbonate may be used to advantage. In all cases the neutralizing reagent should be in a state of considerable dilution to avoid the possibility of undesirable action on the oil phase of the emulsion.

In place of any oil-insoluble reagent such as those above mentioned I prefer to use a reagent which is a naturally occurring constituent of petroleum and is miscible with the oil phase, through which it is transmitted to the water phase of the emulsion. Such reagents are, for example, the naphthenic acids for the correction of waters having a hydrogen ion concentration represented by a pH value materially greater than 5.2, and quinoline and/or pyridine bases for the correction of acid waters. These substances may be utilized in the more or less impure form in which they are recovered from petroleums containing them, provided each batch be standardized to determine its neutralizing value.

I have also discovered that the reagents last named may be utilized to great advantage in the laboratory determination of the water content of petroleums containing emulsified water, as in the standard A. S. T. M. method D 96–35. This method includes the step of diluting the oil with a solvent such as benzol, "bisulpholine," or "phenoline," i. e., of any petroleum solvent which is substantially insoluble in water. I have found that by the addition to these solvents of naphthenic acid or a petroleum base, preferably with a further addition of a trifling quantity of a sulfonated ester, the separation of the water is materially accelerated and the test affords results comparable in accuracy with the determination of water by distillation. The sulfonated ester, which functions as a wetting-out agent, should be oil soluble and only slightly water soluble. The formulae which I prefer to use are approximately as follows:

A.—*For crudes containing alkaline waters*

1.0% to 1.5% "Aerosol OT" or other sulfonated ester
0.5% to 1.5% mixed naphthenic acids
Commercial 90% benzol or other petroleum solvent, to make 100%

B.—*For crudes containing acid waters*

1.0% to 1.5% "Aerosol OT" or other sulfonated ester
0.5% to 2.0% pyridine and/or quinoline bases
Commercial 90% benzol or other petroleum solvent, to make 100%

"Aerosol OT," a wetting-out agent available from the American Cyanamid Company, is the di-octyl ester of sodium sulpho-succinate.

In applying these solvents the pH of the water in the sample to be tested may be determined, if not already known, or parallel samples may be dissolved in the two solvents and the results read

only on the one which gives a sharp indication.

In the use of the mineral or the oil-insoluble reagents it is necessary to adjust the dosage very closely in order to bring the pH of the water within the range specified, as obviously an excess will carry the hydrogen ion concentration past the optimum value. When the oil soluble organic acids and bases are used, it is not necessary to control the dosage so closely as while the neutralization of, for example, an alkaline water by naphthenic acids is accomplished rapidly, the solubility of these acids (and similarly of the petroleum bases) in neutral water is so slight that solution substantially ceases or becomes very slow, when the point of neutrality is reached.

In the use of the above formulae A or B in testing petroleum for its water content, the combination of the wetting agent ("Aerosol" or its equivalent) with a large volume of a limpid solvent eliminates the necessity for any further treatment to resolve the emulsion and permit the water to stratify in the centrifuge. For the commercial resolution of petroleum emulsions, however, it will be understood that the above described step of bringing the pH of the contained water within the optimum pH range is not itself sufficient, in most cases, to effect resolution of the emulsion and separation of the water, but that it is to be followed by any preferred emulsion breaking treatment, which may be chemical or electrical and with the application of heat if required. In other words, this step will be found useful mainly in accelerating and rendering more complete the action of any of the conventional methods of emulsion resolution and its use will be found to result in material savings in treating time, chemicals, electrical current and/or heat, besides producing a lower M. & B. S. cut in the final product than ordinarily can be had otherwise. (The term "M. & B. S." denotes the total of impurities non-miscible with oil and of greater specific gravity, including concentrated unresolved emulsion.)

I claim as my invention:

1. In the treatment of petroleum emulsions: the step of bringing the hydrogen ion concentration of the water of said emulsion within the range pH 5.5 to pH 4.8 by adding to said emulsion a reagent capable of neutralizing the excess acidity or alkalinity of said water.

2. In the treatment of petroleum emulsions: the step of bringing the hydrogen ion concentration of the water of said emulsion within the range pH 5.5 to pH 4.8 by adding to said emulsion a volatile reagent capable of neutralizing the excess acidity or alkalinity of said water.

3. In the treatment of petroleum emulsions in which the hydrogen ion concentration of the water of said emulsion numerically exceeds pH 5.5, the step of bringing the hydrogen ion concentration of said water within the range pH 5.5 to pH 4.8 by adding naphthenic acid to said emulsion.

4. In the treatment of petroleum emulsions in which the hydrogen ion concentration of the water of said emulsion numerically exceeds pH 5.5, the step of bringing the hydrogen ion concentration of said water within the range pH 5.5 to pH 4.8 by adding an oil soluble acid to said emulsion.

5. In the treatment of petroleum emulsions in which the hydrogen ion concentration of the water of said emulsion is numerically less than pH 4.8, the step of bringing the hydrogen ion concentration of said water within the range of pH 5.5 to pH 4.8 by adding petroleum bases to said emulsion.

6. In the treatment of petroleum emulsions in which the hydrogen ion concentration of the water of said emulsion is numerically less than pH 4.8, the step of bringing the hydrogen ion concentration of said water within the range of pH 5.5 to pH 4.8 by adding to said emulsion a basic body selected from the group consisting of the pyridines and the quinolines.

7. In the treatment of petroleum emulsions in which the hydrogen ion concentration of the water of said emulsion is numerically less than pH 4.8, the step of bringing the hydrogen ion concentration of said water within the range pH 5.5 to pH 4.8 by adding an oil soluble base to said emulsion.

8. A composition for diluting petroleum to cause the separation of water therefrom, from petroleum consisting substantially of a water-insoluble petroleum solvent together with from 1.0% to 1.5% by weight of a sulphonated ester only slightly soluble in water and from 0.5% to 1.5% by weight of naphthenic acid.

9. A composition for diluting petroleum to cause the separation of water therefrom, consisting substantially of a water-insoluble petroleum solvent together with from 1.0% to 1.5% by weight of a sulphonated ester only slightly soluble in water and from 0.5 to 2.0% by weight of a basic substance selected from the group consisting of the pyridines and the quinolines.

10. In the treatment of petroleum emulsions: the step of bringing the hydrogen ion concentration of the water of said emulsion within the range pH 5.5 to pH 4.8 by adding to said emulsion an oil-soluble reagent capable of neutralizing the excess acidity or alkalinity of said water.

ABRAHAM SHAPIRO.