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FILTERING OIL SOLUTION OF CALCIUM SULFONATE USING A SYNTHETIC POLYELECTROLYTE

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The present invention relates to an improved method of removing finely-divided, insoluble materials from liquids. It especially concerns the removal of suspended sediment and insoluble matter from mineral oil and mineral oil solutions. The invention has particular application to the manufacture of alkaline earth metal sulfonates where it is necessary to filter insoluble metal sulfates and the like from mineral oil solutions of alkaline earth metal sulfonates.

The problem of removing finely divided solids and other insoluble materials from liquids is well known in the chemical art. It is of particular importance to the petroleum industry where it is often necessary to remove undesirable insoluble materials from the feed stocks to various refining operations as well as from the refined products that are derived therefrom. For example, the petroleum refiner generally finds it necessary or desirable to filter, settle or similarly treat petroleum crude oils in order to remove insoluble metal salts, metal oxides, various metallo-organic compounds, etc. from the oils. It has been the experience of the petroleum industry that such materials, unless removed, give rise to serious problems in different refining operations that are performed on the oils. Some of the materials cause corrosion of refining equipment, while others tend to poison or otherwise impair the activity of various catalytic and chemical refining agents.

The petroleum refiner, as mentioned above, has also found it necessary frequently to remove insoluble, suspended materials from various petroleum products as well as refining intermediates. Thus, it is frequently necessary to separate brine, metal salts, metal oxides and similar materials from bunker fuel oils and other residual products. Consumers of such products have found that these and other insoluble contaminants are often injurious to the equipment in which they are eventually employed.

In considering conventional petroleum feed stocks and refined products, it is well to note that there are a number of accepted standard analytical procedures for measuring or otherwise determining the amounts of sediment that are contained therein. One of the best known of these procedures is one that has been advanced by the American Society for Testing Materials and is identified as ASTM Test Procedure D96–52T.

In addition to handling conventional petroleum feed stocks and products, the modern petroleum refiner is further confronted with the problem of removing insoluble contaminants from various petrochemicals, petroleum derivatives and petroleum additives. This is particularly true in the manufacture of products such as the metal salts of petroleum sulfonic acids, the metal salts of alkyl phenol sulfides, the metal salts of naphthenic acids, the metal salts of polypropyl benzene sulfonic acids, synthetic polymeric lubricating oils, synthetic polymeric turbine oils, and the like. These products are generally prepared in mineral oil solution, and a necessary step in their preparation and purification

is the removal of insoluble metal salts and other impurities from the final or intermediate products.

A number of procedures have been employed and are still employed by the petroleum industry for removing insoluble materials from the aforementioned petroleum feed stocks, refined products, petrochemicals, etc. These procedures include operations such as decantation, centrifuging, settling, electrolytic precipitation, etc. While the present invention has application to all of these procedures, it has particular application to the process of filtration wherein a mineral oil or mineral oil solution containing insoluble matter is passed alone or in admixture with a conventional diatomaceous earth-type filter aid through filter mediums such as filter cloths, perforated plates, beds of finely divided solids, or the like. And of these various filter mediums the present invention is especially suited for use in conjunction with filter cloths.

Filter cloths are commercially available in a wide variety of weaves and fabrics and are generally used either in plate and frame filter presses or in rotary type filters. As mentioned above, they have found wide application in the petroleum industry for removing suspended or finely divided solid matter from petroleum feedstocks, refined products, petrochemicals, etc. In connection with these operations, however, it has been observed that the filter cloths tend to plug or "blind" very rapidly with the result that satisfactory filter rates are often difficult to maintain. It is generally considered that the finely divided insoluble matter in the feed to a filter fills up the pores of the filter cloth employed therein and thereby reduces the rate of filtration. This condition is also true of the performance of the other types of filter mediums described earlier herein.

Accordingly, it is an object of the present invention to provide an improved process for filtering finely divided solids and other insoluble materials from mineral oils and mineral oil solutions of oil soluble metal salts, soaps, and the like.

This and other objectives may be realized in accordance with the present invention by incorporating within the feed stock to a filtering operation a small amount of a particular type of filter aid. In accordance with the present invention, a very minor proportion of a synthetic polymeric, water-soluble polyelectrolyte having a molecular weight of at least 10,000 and containing a substantially linear continuous carbon chain derived by the polymerization of an aliphatic unsaturated group is added to the feed stock. Additives of this character and their preparation have been described at length in the prior art and especially in U. S. 2,625,529 issued to Hedrick and Mowry. The polyelectrolytes that are described in that patent embrace the additives that are suitable for the practice of the present process.

In the present invention it is particularly contemplated that about 0.001 to 0.10 wt. percent of a polymeric polyelectrolyte be added to a feed stock which is about to be filtered. It is particularly desirable to employ a concentration of the order of about 0.01 wt. percent.

It is further preferred that the polymeric polyelectrolyte have a molecular weight in excess of about 15,000. The optimum molecular weight of some polymers may be as high as 30,000 to 100,000.

It is contemplated that the best method of practising the present invention consists in adding the polyelectrolyte in finely-divided solid form to the filtering feed stock, thoroughly mixing the two materials, and thereafter passing the feedstock through the filter. The operation may be either continuous or batch-type in operation. It is particularly preferred that a conventional amount (i.e. of the order of about 0.01 wt. percent) of diatomaceous

earth also be mixed in with the feedstock or applied as a precoat to the surface of the filter medium.

Additives which are particularly suitable for the purposes of the present invention include the equimolar copolymers of vinyl acetate and a polycarboxylic acid derivative. The polycarboxylic acid derivative may be maleic acid, maleic anhydride, the amides and substituted amides of maleic acid and the ammonium, alkali metal or alkaline earth metal salts of these acids. Specific examples of suitable polycarboxylic acid derivatives include maleic acid, maleic anhydride, sodium maleate, potassium maleate, ammonium maleate, calcium maleate, monosodium maleate, maleic acid amide, sodium maleamate, ammonium maleamate, etc. Other particularly suitable polycarboxylic acid derivatives include the monoalkyl esters of maleic acid and the aminoalkyl esters and half esters of maleic acid.

The copolymers of vinyl acetate and the above-mentioned polycarboxylic acid derivatives may be prepared in different ways. For example, they may be prepared by direct polymerization of the various monomers; or they may be prepared by an after-reaction of other copolymers. An additive that is contemplated to be particularly suited for the practice of the present invention is the equimolar copolymer of vinyl acetate and monosodium maleate having a molecular weight in excess of about 15,000 and especially of the order of about 30,000.

Other particularly attractive copolymers for use in practising the present invention include vinyl acetate-diammonium maleate; vinyl acetate-maleic acid, triethanolamine salt; vinyl acetate-maleic acid β-dimethylaminoethyl half-ester; and vinyl acetate-ammonium maleamate. It will be observed that these copolymers are identified in terms of their monomeric constituents. The names so applied refer to their molecular structure and are not limited to the polymers prepared by the copolymerization of the specified monomers.

The copolymers that are employed in the present process are water-soluble in that they form homogeneous mixtures with water or in that they expand in the presence of water and dissolve to at least some extent. This characteristic of water-solubility is considered to have some relationship to the success of the present invention, although the exact nature of the phenomenon involved is not known. It has been observed that the presence of small amounts of moisture in the material to be filtered proves beneficial to the filtration procedure.

It will be noted that most of the liquids that have been referred to earlier herein characteristically contain small amounts of water up to about 15 parts per 100 parts of liquid. It is contemplated that the process of the invention is most effective when the feed to a filtering operation contains about 0.1 to 1.0 wt. percent water. Thus, it may be desirable in some instances to add sufficient water to a given feedstock to provide it with this amount of moisture. This addition may be separate from or concurrent with the addition of the polymeric polyelectrolyte. Subsequent to the filtration, the moisture may be removed from the filtrate in any desired conventional manner.

The present invention may be better understood by reference to the following example wherein one of the polymeric polyelectrolytes named above was employed to aid in the filtration of a mineral oil solution of calcium sulfonate which had been derived in turn from the sulfonation and subsequent neutralization of a lube oil stock. The manufacture of calcium petroleum sulfonate by such a procedure is well known in the art, and a detailed discussion of this process is not considered to be necessary in the present description.

It will be briefly noted, however, that calcium sulfonate is conventionally formed by treating a selected lube oil stock with oleum which reacts with hydrocarbons in the lube oil to form sulfonic acids. The resulting sulfonic acids are neutralized and converted to sodium sulfonates by treatment with a solution of sodium carbonate or other alkali, generally in the presence of isopropyl alcohol. The resulting solution of sodium sulfonate is then treated with strong isopropyl alcohol of about 85–91 wt. percent concentration to rid the solution of any undesirable metal salts such as sodium sulfate, sodium carbonate, sodium sulfite, etc.

The resulting desalted solution of sodium sulfonate in isopropyl alcohol is blended with a good quality neutral lube oil fraction and distilled to form about a 50% solution of sodium sulfonate in oil. The sodium sulfonate is then converted to calcium sulfonate by treatment with an excess of calcium chloride in the form of a concentrated brine solution. The resulting calcium sulfonate product conventionally contains very substantial amounts of calcium chloride, sodium chloride, water, calcium sulfate, calcium sulfite, calcium carbonate, etc. which must be removed from the calcium sulfonate product. Lime is then added to this solution and most of the water is removed by dehydration in a tank equipped with coils and maintained at about 300° F. The remaining insoluble salts are then removed from the calcium sulfonate product by filtering the product through a conventional filter press or rotary filter. The feed to the filter may contain from about 0.1 to 8 wt. percent water and generally contains about 0.1 to 1%. A conventional amount of water is about 0.3%.

To illustrate the present invention, separate portions of a calcium sulfonate solution containing of the order of about 1% water and the aforementioned insoluble materials were separately filtered through a conventional cloth filter medium. The filter was precoated with about 0.06 wt. percent (based on the solution) of a conventional diatomaceous earth filter aid. One of the portions contained no additive, while the other portion contained about 0.01 wt. percent of the vinyl acetate-monosodium maleate copolymer described hereinbefore. Each of the portions was passed through the filter, and the volume of filtrate obtained was determined at regular intervals in each case. The results of these tests are presented in the following table:

Effect of polymeric polyelectrolyte on the filterability of a calcium sulfonate-oil solution

Quantity of Polyelectrolyte added, Wt. Percent	None	0.01
Calcium Sulfonate Filtrate Volume, ml.:		
After 1 Minute	50	65
After 2 Minutes	90	125
After 5 Minutes	155	230
After 10 Minutes	240	345
After 20 Minutes	350	495
After 30 Minutes	410	600
Percent Increase after 30 Minutes		48.0

It is apparent from the above table that the present additives constitute very effective filter aids in filtering oil solutions of calcium sulfonate that contain insoluble matter in the form of metal salts and the like. It will be noted, however, that these results are merely intended to serve as an illustration of the present invention, and the invention is not to be considered to be limited to this particular example. It is contemplated, for example, that the invention has application to other separation processes such as centrifuging, settling, decanting, etc. and to other feedstocks such as residual fuel oils, synthetic lubricating oils, etc.

The data in the above table were obtained on a solution of calcium sulfonate in which the solution had a water content of about 0.3 wt. percent, the sulfonate an average mol. wt. of about 925, and the solvent was a solvent-extracted coastal stock of 40 S.S.U. @ 210° F. It is considered, however, that sulfonate solutions of different mol. wts., different solvents, etc. would be just as effectively improved.

What is claimed is:

1. The method of removing insoluble finely divided

matter from an oil solution of calcium sulfonate containing about 0.1 to 1.0 wt. percent of water which comprises incorporating within the oil solution about 0.001 to 0.10 wt. percent of a synthetic, polymeric water-soluble polyelectrolyte having a mol. wt. of at least 10,000 and containing a substantially linear continuous carbon chain derived by the polymerization of an aliphatic unsaturated group, and thereafter passing the solution through a filter whereby the insoluble matter is separated from the solution.

2. A method as defined in claim 1 in which the polyelectrolyte is a copolymer having the structure of a copolymer of vinyl acetate and monosodium maleate.

3. A method of improving the filterability of finely divided matter from a mineral oil solution of calcium sulfonate which comprises incorporating within the mineral oil solution about 0.001 to 0.10 wt. percent of a synethetic water-soluble polyelectrolyte having an average molecular weight of at least 10,000 and a structure derived by the polymerization of at least one monoolefinic compound through the aliphatic unsaturated group, said structure being substantially free of cross-linking.

4. A method as defined in claim 3 in which the polyelectrolyte has a molecular weight in excess of about 15,000.

5. A method of improving the filterability of finely divided matter from a mineral oil solution of calcium sulfonate which comprises incorporating within said liquid about 0.001 to 0.10 wt. percent of a synthetic polymeric water-soluble polyelectrolyte having a molecular weight of at least 10,000 and containing a substantially linear continuous carbon chain derived by the polymerization of an aliphatic unsaturated group.

6. A method of improving the filterability of a mineral oil solution containing calcium sulfonate, finely divided and insoluble matter and up to about 15 parts per hundred of water which comprises incorporating within the mineral oil solution about 0.001 to 0.10 wt. percent of a synthetic polymeric water-soluble polyelectrolyte having a molecular weight of at least 10,000, said polyelectrolyte being a copolymer of vinyl acetate and a polycarboxylic acid derivative.

7. A method as defined in claim 6 in which the polycarboxylic acid derivative is selected from the class consisting of maleic acid, maleic anhydride, the amides and substituted amides of maleic acid and the ammonium, alkali metal and alkaline earth metal salts of maleic acid and the monalkyl and the amino alkyl esters and half esters of maleic acid.

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