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VISCOSITY REDUCTION OF PETROLEUM MAHOGANY SULFONATE HYDROCARBON SOLUTIONS

Abraham Moscowitz, New York, N. Y., assignor to L. Sonneborn Sons, Inc., a corporation of Delaware

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9 Claims. (Cl. 260—504)

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This invention relates to new and useful improvements in the viscosity reduction of petroleum mahogany sulfonate hydrocarbon solutions.

Petroleum mahogany sulfonate solutions in organic solvents of the water immiscible type are used for a variety of purposes such as wetting agents, emulsifying agents and the like. Ordinary petroleum mahogany sulfonates impart to their solutions a relatively high viscosity. In some cases this high viscosity is not critical regarding the purpose for which the sulfonate solutions are to be used. There are, however, many cases in which a relatively high viscosity is undesirable or detrimental to their intended use or application. This is, for example, true in textile processing such as of wool, worsted, rayon, viscose or the like in which the various processing steps involved in the conversion of the raw materials into fibres, the formation of the fibres into threads and the weaving of the threads into fabric, require the presence of a lubricating agent having a Saybolt viscosity of below 600 and preferably below 300 seconds Saybolt at 100° F. The latter is particularly true of textile lubricants used in the processing of synthetic fibres. In the case of textile processing it is for instance desirable to have a hydrocarbon textile lubricant composition with a sulfonate content of in excess of 28% mahogany sulfonates so as to render the composition not only readily and spontaneously emulsifiable but also to make the same readily wettable or rewettable on the fibre to thereby impart to the textile material substantial self-scourability. Hydrocarbon solutions of the textile lubricant type and containing in excess of 28% of petroleum mahogany sulfonates possess, however, a viscosity far in excess of 600 seconds Saybolt at 100° F. and usually a viscosity in excess of 1000 seconds Saybolt at 100° F. For this reason it has been necessary in the past in such cases to limit the sulfonate content to a maximum of approximately 15% in order not to exceed the usable viscosity for textile material treating purposes. Another example is the use of petroleum mahogany sulfonates in the compounding of cutting oil bases in which the relatively high viscosity and tackiness imparted to the composition by the sulfonates is an undesirable aspect interfering in many respects with the proper ease of application and use.

The relatively high viscosity of petroleum mahogany sulfonates in organic solvents is normally not subject to reduction by the addition of relatively low viscous diluents or thinning agents. This requires agents of such relatively low

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viscosity that they interfere with the lubricating properties of the composition. Furthermore, these solvents are then of the type which easily evaporate. This is particularly critical in the case of textile treating materials since the use of such thinning solvents will leave behind on the fibre upon evaporation a viscous sticky impregnant without adequate lubricating capacity on the fibre and will also interfere with the scourability of the impregnated material. On the other hand, thinning with a solvent of the lubricant type diluent will not obtain the desired result as it is necessary to add so much of the diluent as to bring the sulfonate content to below that necessary for adequate emulsification or other purpose for which the composition is designed.

One object of the invention comprises inter alia the viscosity reduction of a petroleum mahogany sulfonate organic solvent solution. This and further objects of the invention will appear from the following description.

In accordance with the invention, a suitable petroleum mahogany sulfonate solution in an organic substantially water immiscible solvent for said sulfonate is reacted at a neutral to alkaline pH with chlorine dioxide in amount and for a period of time sufficient to appreciably lower the viscosity of said solution and preferably by at least one-third.

The solvents that may be used for this purpose should be substantially neutral to chlorine dioxide action and should be substantially liquid at normal temperatures. Suitable solvents that may be used in the practice of the invention are, for instance, petroleum oil distillates or any fraction thereof, benzol and its homologs, naphtha, carbon tetrachloride, tetrachlorethane, chloroform, etc., and in general any aromatic or aliphatic or aryl or aralkyl hydrocarbon or hydrocarbon mixture including their halogenated derivatives of the aforedescribed character and nature. In many cases, particularly where the solvent is to be removed after the viscosity reducing treatment, it is desirable to have the boiling range of such solvent sufficiently low to permit removal in the customary manner such as by distillation in vacuo or otherwise without causing thereby decomposition of the mahogany sulfonates. In such cases it is of advantage that the boiling point be so low and preferably between 75 and 250° F. as to enable the removal of the solvent at ordinary temperatures without the necessity of resorting to vacuum distillation.

The petroleum mahogany sulfonate which is

subjected to the viscosity reduction is normally one derived from the acid refining, with fuming sulfuric acid, of a petroleum oil distillate stock under sulfonating conditions of acid amount and temperature in accordance with conventional refining practice. In such conventional fuming sulfuric acid refining an oil layer and acid sludge layer are formed, the former containing dissolved therein pertoleum mahogany sulfonic acids collectively referred to as mahogany petroleum sulfonic acids. These are recovered from the oil layer in accordance with conventional methods in the form of solutions of these sulfonic acids or their salts (the latter being collectively termed "petroleum mahogany sulfonates") in a portion of the oil relatively tenaciously occluded by these sulfonic bodies. This occluded oil is generally referred to in the art as "retained" oil. The petroleum sulfonic acids or sulfonate oil compositions normally contain about 30 to 35% of retained oil and 65 to 70% of the petroleum mahogany sulfonic material. Depending upon the type and origin of petroleum oil distillates from which these sulfonate-oil solutions or stocks are derived they contain sulfonates of varying averaged molecular weights. For convenience therefore the sulfonate stocks are identified by their average molecular weights. Thus, a 420 or 450 sulfonate stock is a stock in which the sulfonates have an average molecular weight of 420 or 450 respectively.

In the practical application of the invention, the crude mahogany sulfonate in the organic solvent solution is contacted with the chlorine dioxide by, for instance, passing the same into or through the solution until the desired viscosity reduction is obtained which may be ascertained by the drawing of periodic samples and the examination thereof on a suitable viscosimeter. Viscosity reduction is usually accompanied by color decrease which is particularly of advantage when the composition is intended for a use in which its tinctorial value is of importance as, for instance, for textile use. Color reduction to a Lovibond color value (10% white oil solution ½ inch cell) of less than 8R and preferably down to 2–3R is usually desirable in such cases.

The chlorine dioxide is preferably obtained by generating the same in a suitable generator such as by the interaction of chlorine and sodium chlorite. A suitable chlorine dioxide generator arrangement is, for instance, one in which chlorine is passed through a stoneware or glass-lined tower 4 inches in diameter and 3½ feet high, filled with dry commercial flaked sodium chlorite. The chlorine is fed therethrough at the rate of 0.05 to 1.5 cubic feet per hour in admixture with a large excess of air at a positive pressure between 2 and 5 lbs. per square inch in excess of atmospheric. This admixture is introduced into the bottom of the tower and the chlorine dioxide formed within the tower is carried out at the top by the positive air stream. The mixture of chlorine dioxide and air is then preferably passed to the base of a second similarly constructed and charged reaction tower and emerges from the top into a gas manifold from which it is conducted into the sulfonate solution to be treated. Exhaustion of the chlorite in a tower is indicated when appreciable amounts of chlorine begin to accompany the chlorine dioxide issuing from the tower. At maximum output the rate of chlorine dioxide in the gas emerging from the reaction tower is better than 80% and may reach as high as better than 95%. The second tower serves primarily to maintain continuity of the reaction and provision is made to cut out the first tower for recharging when its chlorite content approaches exhaustion, leaving the second tower temporarily as the sole operating unit. It is of course understood that the chlorine dioxide may be generated in any other manner whether by way of a dry process or a wet process basically involving a reaction in accordance with the following equation: $2NaClO_2$ plus Cl_2 equals 2NaCl plus $2ClO_2$.

The chlorine dioxide reaction or treatment may be carried out at a pH of from 7 to 9 and preferably of from 8 to 8.5. If necessary the solution may be alkalized with a suitable alkaline agent such as caustic soda to the desired pH. It is recommended that excess alkalinity be avoided as it may be detrimental to the efficiency of the viscosity reduction and may furthermore give rise to an undesirable partial decomposition of the sulfonates.

When proceeding in accordance with the invention it is recommended and sometimes necessary that the petroleum mahogany sulfonate hydrocarbon solution be ultimately contacted with the chlorine dioxide in the presence of relatively small amounts of water. Normally a minimum of about 1 to 1.5% of water by weight of sulfonate in solution will suffice for this purpose. Ordinarily larger amounts of water are not critical except to the extent that they might constitute an unnecessary diluent for the reactants, thus impeding the ready viscosity reduction of the solution.

It is also recommended and sometimes necessary in the practice of the invention that the viscosity reducing reaction is carried out in the presence of relatively small amounts of an electrolyte, i. e., any compound ionizable in the medium in which the treatment is carried out, to impart electrical conductivity to the medium. Most substantially water soluble organic and inorganic bases and salts are such electrolytes. In the majority of cases petroleum mahogany sulfonates have a certain inorganic salt content, mostly composed of alkali sulfates and sulfites in the order of ½ to 5 and usually 2 to 2½%. These suffice and no further addition of electrolyte is necessary. In the event, however, that exceptionally pure, i. e., salt free sulfonate, is to be subjected to the treatment in accordance with the invention, it may be of advantage to add small amounts of an electrolyte such as 0.5 to 3% of NaCl, Na_2SO_4, or other suitable electrolyte material (by weight of the sulfonate present in solution). For the purpose of obtaining the best effect of the electrolyte and carrying out viscosity reducing reaction in accordance with the invention, it is preferred to proceed in the presence of relatively small amounts of water of the order hereinabove mentioned and as there may be, for example, present in conventional sulfonate stocks, i. e., 0.5 to 1% of water by weight of sulfonate in solution. Excess amounts of electrolyte are not critical though they may entail the inconvenience of salt removal steps provided, of course, that when a strongly alkaline reacting electrolyte is present care should be taken that the maximum alkalinity for efficient operation is not exceeded.

The temperature of reaction is ordinarily not critical. The reaction, however, may be facilitated by increasing the temperature to, for example, a preferred temperature of from 120 to 200° F. This is particularly desirable with more

heavily viscous solutions as the higher temperature will increase the fluidity of the solution, thus permitting more intimate contact between the reactants.

The extent to which low viscosity values may be obtained depends, at least to some extent, upon the type or origin of the petroleum mahogany sulfonate selected for the treatment. Ordinarily higher average molecular weight sulfonates possess a higher viscosity and the resulting viscosity after treatment is usually commensurately higher than the viscosity after treatment of a comparative sulfonate hydrocarbon solution which before treatment possessed a relatively lower viscosity and in which the sulfonate had a lesser average molecular weight.

The ratio of petroleum mahogany sulfonate to solvent is, as a rule, not critical except that it is desirable to so adjust the ratio that the viscosity of the solution is sufficiently low at the desired or selected temperature of treatment to permit the intimate contact between the reactants. In most cases, however, a ratio of mahogany sulfonate to solvent of substantially 2 to 1 (by weight) will give satisfactory results. Sulfonate concentrations above 70 to 75% sulfonate content are normally not desirable for direct reaction without suitable extension. As a mode of agitation, any conventional method such as stirring, air-blowing, shaking, etc., may be used.

As above pointed out, the viscosity reducing reaction in accordance with the invention may be carried out with an organic solvent solution containing relatively high concentrations of petroleum mahogany sulfonate. In this case the resultant product is a concentrate which in many cases must be thereafter adjusted by the addition of organic solvent material of suitable viscosity, such as a suitable lubricant hydrocarbon, to the requisite petroleum mahogany sulfonate content desired for the specific purpose for which the composition is to be used. Thus, for instance, if it is desired to ultimately produce a textile treating oil having in excess of 28% petroleum mahogany sulfonate and a viscosity of less than 600 seconds Saybolt at 100° F., a concentrate having in excess of 40% and usually between 60 and 65% sulfonate, is first obtained after the viscosity reducing reaction in accordance with the invention, which product may be then extended by the addition of a suitable lubricant hydrocarbon such as a mineral pale oil having a viscosity of 75 seconds Saybolt at 100° F. to a sulfonate content between 28 and 40% and a viscosity below 600 seconds Saybolt at 100° F.

Alternatively, the viscosity reducing reaction may be carried out with an organic solvent solution of a petroleum mahogany sulfonate already possessing the requisite final sulfonate content desired and intended for the purpose for which the viscosity reduced product is to be used. In that case it is also of advantage to select for the solution such solvent as is desired for the final product, i. e., if a textile lubricating oil is intended to be ultimately obtained a textile lubricant, having for instance a viscosity between 40 and 150 seconds Saybolt at 100° F. is selected as the solvent for the sulfonate. The product resulting from the viscosity reducing treatment is then per se usable after such further refining or purification as may be required for a textile treating oil.

Though in the operation of the novel viscosity reducing process any of the aforementioned solvents may be used with advantage, I prefer to use as the solvent that hydrocarbon fraction, the acid refining of which furnished the crude mahogany sulfonate stock and which is carried as "retained" oil. The crude mahogany sulfonate-retained oil stock constitutes as such a convenient mahogany sulfonate solution that may be subjected directly to treatment in accordance with the invention.

Once a petroleum mahogany sulfonate has been subjected in suitable solvent medium to a viscosity reducing reaction in accordance with the invention, it is possible to remove the solvent if desired and recover the petroleum mahogany sulfonates as such substantially free from solvent. These sulfonates when redissolved in the solvent still exhibit in solution the same reduced viscosity which they possessed prior to the removal of the solvent.

The following examples are furnished by way of illustration and not of limitation:

Example I

100 lbs. of a petroleum mahogany sulfonate stock containing about 62% sulfonate and about 35.5% "retained" oil was used. The stock was obtained from a mid-Continent distillate subjected to white oil refining with fuming sulfuric acid under sulfonating conditions in the conventional manner. The mahogany sulfonates in the stock possessed an average molecular weight of 450. The stock possessed a Furol viscosity of 132 at 210° F. and upon extension with a mineral pale oil (75 seconds Saybolt at 100° F.) to a 30% sulfonate content a viscosity of 1322 seconds Saybolt at 100° F. The H_2O content of the stock was about 1.5% by weight of the sulfonates in solution.

The non-extended sulfonate stock was then adjusted to a pH of 8.5 with the addition of a 5% aqueous caustic soda solution. Chlorine dioxide was then slowly passed into the stock at a temperature for the stock of about 180° F. The chlorine dioxide was obtained from a chlorine dioxide generating tower using chlorine and dry flaked sodium chlorite as hereinabove described. The stock was agitated while the chlorine dioxide was passed into the same and the treatment was continued until a sample exhibited a Furol viscosity of about 52 at 210° F. Upon extension to a 30% sulfonate content with the aforementioned 75 viscosity mineral pale oil, a viscosity of about 450 seconds Saybolt at 100° F. was noted.

Example II

The petroleum mahogany sulfonate stock specified in Example I was subjected to a de-oiling process in accordance with conventional practice. 30 parts by weight of the resultant oil-free petroleum mahogany sulfonate was then dissolved in 70 parts by weight of benzol. The solution possessed a Saybolt viscosity of about 950 seconds at 100° F.

This solution was then adjusted to a pH of 8.5 with the addition of a 5% aqueous caustic solution and chlorine dioxide was slowly passed into the solution. The solution was agitated while the chlorine dioxide was passed into the same and the treatment was continued until a sample exhibited a Saybolt viscosity of about 420 seconds at 100° F.

The reacted solution was then distilled for removal of the solvent and the resultant sulfonate was dissolved in a 75 viscosity mineral pale oil to yield a 30% sulfonate content oil solution. This solution had a viscosity of about 450 seconds Saybolt at 100° F.

Example III

The same de-oiled petroleum mahogany sulfonate as specified in Example II was dissolved in carbon tetrachloride to yield a 30% sulfonate content solution. This was then subjected to chlorine dioxide treatment in a manner set forth in Example II until the sample exhibited a Saybolt viscosity of 1120 seconds at 100° F.

The solvent-stripped sample when dissolved in a 75 viscosity mineral pale oil to yield a 30% oil solution possessed a viscosity of 450 seconds Saybolt at 100° F.

The foregoing description is for purposes of illustration and not of limitation and it is therefore my intention that the invention be limited only by the appended claims or their equivalents wherein I have endeavored to claim broadly all inherent novelty.

I claim:

1. Process for reducing the viscosity of petroleum mahogany sulfonate solutions which comprises treating a petroleum mahogany sulfonate solution in an organic substantially water immiscible solvent for said sulfonate at a neutral to alkaline pH substantially of from 7 to 9 with chlorine dioxide in amount and for a period of time sufficient to appreciably reduce the normally relatively high viscosity of said solution due to the sulfonate dissolved therein to a point sufficiently low to yield for a 28–40% solution of said sulfonate in a petroleum hydrocarbon a viscosity below 600 seconds Saybolt at 100° F. said solvent being substantially inert to the action of chlorine dioxide.

2. Process in accordance with claim 1 in which said solution is treated in the presence of at least 0.5% of an electrolyte and of at least 1 to 1.5% of water by weight of sulfonate in solution.

3. Process according to claim 2 in which said solution is treated with said chlorine dioxide in amount and for a period of time sufficient to reduce said normally relatively high viscosity of said solution by at least one third.

4. Process in accordance with claim 3 in which said solution is a petroleum mahogany sulfonate solution in "retained" oil.

5. Process in accordance with claim 4 in which said solution is treated at a pH substantially of from 8 to 8.5.

6. Process for reducing the viscosity of petroleum mahogany sulfonate solutions which comprises treating a solution of in excess of 28% petroleum mahogany sulfonate in a solvent for said sulfonate of the petroleum hydrocarbon type having a viscosity substantially between 40 and 150 seconds Saybolt at 100° F., at a pH of substantially from 7 to 9 and in the presence of at least 0.5% of an electrolyte and at least 1 to 1.5% of water by weight of sulfonate in solution with chlorine dioxide in amount and for a period of time sufficient to reduce the normally relatively high viscosity of said solution due to the sulfonate dissolved therein to a point sufficiently low to yield for a sulfonate content in excess of 28% a viscosity below 600 seconds Saybolt at 100° F.

7. Process for reducing the viscosity of petroleum mahogany sulfonate solutions which comprises treating a solution in excess of 40% petroleum mahogany sulfonate in "retained" oil at a pH of substantially from 7 to 9 and in the presence of at least 1 to 1.5% of water by weight of sulfonate in solution with chlorine dioxide in amount and for a period of time sufficient to reduce the relatively high viscosity of said solution due to the sulfonate dissolved therein to a point sufficiently low to yield upon extension to a 28 to 40% sulfonate content with a solvent of the petroleum hydrocarbon type having a viscosity of from 40 to 150 seconds Saybolt at 100° F., a viscosity of the extended solution below 600 seconds Saybolt at 100° F.

8. Process in accordance with claim 7 in which said solution is treated in the presence of at least 0.5% of an electrolyte.

9. Process in accordance with claim 8 in which said solution is treated at a pH of substantially from 8 to 8.5.

ABRAHAM MOSCOWITZ.

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