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PROCESS FOR OBTAINING COLLOIDAL DIS-PERSIONS OF METALS IN OILS AND **PRODUCTS THEREOF**

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> 20 Claims. (Cl. 252-6)

This invention relates to a new method for obtaining a colloidal dispersion of metals in oil and to new and useful products prepared thereby. This/invention relates more particularly to the

preparation of dispersions of elemental metals in Б oils by dissociation or reduction of metallic soaps of sulfonic acids therein.

When hydrocarbon oils are treated with strong or fuming sulfuric acid there is obtained a class

- of substances which are considered for the pur-10 pose of this invention to be oil-soluble sulfonic acids. These acids and their alkaline salts may be obtained from both the oil and the acid sludge layers, produced on treating oil with sulfuric acid,
- by known methods. For example, the oil layer 15 separated on treating petroleum oil with strong sulfuric acid may be washed with an alcoholic solution of caustic soda and a solution of sodium sulfonates in the alcohol is obtained. The sulfonic acids may be extracted from the oil with 20 an alcohol, such as isopropanol. The acid sludge layer may also be extracted with oil before or after neutralization with an alkali such as caustic soda, potassium hydroxide or ammonia, and sulfonic acids or alkali sulfonates possessing prop-25 erties similar to those obtained from the oil layer are secured.

or dissociation with formation of elemental silver. The silver is obtained according to this method as a colloidal dispersion in the oil. This dispersion is extremely stable as the organic products of the reduction, which may be sulfonic acids or their derivatives, act as efficient protectives and stabilizers for the dispersed metal.

The reduction to form colloidally dispersed metals may be aided by passing a stream of hydrogen gas through the heated oil solution and 10 in this case the reduction proceeds readily at much lower temperatures, even below 100° C. The reduction may be aided by using hydrogen at elevated pressures even up to several hundred atmospheres pressure, when the metallic com-15 pounds are difficultly reducible.

A great variety of other metals may be used in place of silver and this invention is not to be limited to the use of any particular metal since it is applicable to the preparation of metallic dis- 20 persions from substantially all metal compounds which may be reduced to the corresponding metals by hydrogen. By this is meant compounds of metals which are displaceable by hydrogen, that is, metals which are lower in the electromotive $_{25}$ series of metals than is hydrogen. Metallic dispersions may be obtained in a great variety of oils and this invention is especially applicable to all neutral oils of animal, vegetable or mineral origin. For example, dispersions of 30copper may be obtained in white oil or in kerosene and are especially suitable for use as fungicides for application to trees and foliage. Dispersions of lead, selenium and other metals may be obtained readily in gasoline, such dispersions be-35ing of value as antidetonating agents for internal combustion engine fuels. Dispersions of these and other non-abrasive metals in heavy oils may also be used in lubricating oils, greases and the like to especial advantage. Dispersions of bis-40 muth and mercury in various oils are suitable for use in X-ray exploration, sinus localization, and the like. Silver dispersions in oil possess excellent antiseptic qualities while metals such as silver, lead, selenium, bismuth and mercury find $_{45}$ many therapeutic uses such as in the treatment of malignant diseases. In all such metallic dispersions prepared by the above methods the sulfonic acids or their decomposition products, although often occurring in extremely small con- 50 centrations, possess great value as stabilizing agents. The metallic dispersions of suitable metals may also be used as catalysts for various reactions such as hydrogenation, dehydrogenation and the like. 65

The sulfonic acids readily form salts or soaps with heavy metals such as silver, mercury, lead, copper, gold, bismuth, platinum, selenium, tellu-30 rium, and other metals. These metal soaps are generally soluble in oil and when not completely soluble may be readily suspended and dispersed therein by agitation. I have now found that

- when a solution or suspension of these soaps in 35 oil is heated, a dispersion of finely divided elemental metal is obtained in the oil by reduction or decomposition of the soap. The organic decomposition products simultaneously produced are
- retained in solution in the oil and serve as a valuable stabilizing agent for the metallic dispersion.

- My invention will be fully understood from the following example:
- A solution in aqueous alcohol of the sodium 45 salt of oil-soluble sulfonic acids obtained by treating white oil with strong sulfuric acid is treated with a stoichiometric proportion of an aqueousalcohol-soluble silver salt such as silver nitrate. 50 The silver soap thus obtained is washed free of inorganic salts with water. The soap is then dried and dissolved in white oil, a heavy colorless petroleum oil. The oil solution of the silver soap is then heated to a temperature of about 85 or 100
- to 200° C., at which the soap undergoes reduction **5**5

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Additional sulfonic acids may of course be added to the metallic dispersions and the use of oil-soluble sulfonic acids as stabilizing agents for metallic dispersions or sols however prepared 5 is contemplated as being within the scope of this invention. For example, it is known that metallic sols may be obtained by striking an arc between electrodes of the desired metal immersed in a liquid medium. Sulfonic acids may be added 10 to such liquids either before or after the preparation of the sol and are of value in increasing the stability of the sols so produced. It is also known that sols may be prepared by reduction of finely

divided metallic oxides suspended in liquids such 15 as oils. Oil-soluble sulfonic acids are also of value in stabilizing metallic dispersions prepared by this method. ing a salt consisting of said metal and an oilsoluble sulfonic acid in said oil.

9. Process according to claim 8 in which the salt is silver sulfonate.

10. Process according to claim 8 in which the 5 salt consists of silver in combination with an oil-soluble sulfonic acid prepared by treating hydrocarbon oils with strong sulfuric acid.

11. Process for obtaining a heavy metal colloidally dispersed in a hydrocarbon oil compris- 10 ing adding a salt consisting of a metal displaceable by hydrogen and an oil-soluble sulfonic acid to said oil and heating said salt and oil together to a dissociating temperature of the salt.

12. Process according to claim 11 in which the 15 oil and the sulfonic acid salt are heated together to a temperature of approximately 200° C. 13. Process for obtaining a metal colloidally dispersed in a hydrocarbon oil comprising adding a salt consisting of a metal displaceable by hy-20 drogen in combination with an oil soluble sulfonic acid to said oil and reducing the salt in the oil by addition of hydrogen at a reduction temperature. 14. Process according to claim 13 in which 25 the oil and the sulfonic acid salt are heated together to a temperature of about 85 to 200° C. in the presence of free hydrogen. 15. Process according to claim 13 in which the reduction is conducted with hydrogen at super-30. atmospheric pressure. 16. A new process for preparing a colloidal dispersion of a heavy metal in a petroleum hydrocarbon oil comprising preparing a metal soap by reaction in aqueous alcohol of a salt of said metal 35. soluble therein and an alkali salt of oil-soluble sulfonic acid obtained on treating hydrocarbon oils with strong sulfuric acid, drying said soap, preparing a solution of the soap in the hydrocarbon oil and warming said solution to a dissociat- 40ing temperature of the soap.

This invention is not to be limited to any theory regarding the composition of the so-called oil-20 soluble sulfonic acids and sulfonates described herein nor to any examples which are given solely for purpose of illustration, but only by the following claims in which I wish to claim all novelty insofar as the prior art permits.

25 I claim:

1. A new composition of matter comprising a mixture containing oil, a metal colloidally dispersed therein, a stabilizing agent comprising the organic products of dissociation or reduction of 30 an oil soluble sulphonic acid salt of a metal displaceable by hydrogen, and a heavy metal sulfonate of an oil soluble sulfonic acid.

2. A new composition of matter comprising a mixture containing an oil and a heavy metal 35 sulfonate of an oil-soluble sulfonic acid.

3. A new composition of matter comprising a solution in oil of a heavy metal sulfonate of an oil soluble sulfonic acid.

4. A new composition of matter comprising a 40 solution in a petroleum oil of a silver sulfonate of an oil-soluble sulfonic acid.

5. A new composition of matter comprising a mixture containing an oil, a metal colloidally dispersed therein and a stabilizing agent com45 prising the organic products of dissociation or reduction of an oil soluble sulphonic acid salt of a metal displaceable by hydrogen.

6. A new composition of matter comprising a colloidal dispersion of a heavy metal in a hydro-50 carbon oil obtained by reduction of an oil-soluble sulfonic acid salt of said metal in said oil.

7. A new composition of matter comprising a colloidal dispersion of a heavy metal in a hydrocarbon oil obtained by decomposition of a salt consisting of said metal and an oil-soluble sulfonic acid in said hydrocarbon oil.

8. Process for preparing a colloidal dispersion of a heavy metal in an oil comprising dissociat17. Process according to claim 16 in which the solution of soap in oil is warmed to approximately 85 to 200° C.

18. Process according to claim 16 in which the $_{45}$ solution of soap in oil is warmed in the presence of free hydrogen.

19. Process according to claim 16 in which a silver soap is used.

20. A lubricating composition comprising a 50 heavy oil, a non-abrasive heavy metal colloidally dispersed therein and a stabilizing agent of the group consisting of oil-soluble sulfonic acids and salts thereof and the organic products of dissociation or reduction of metal sulfonates of such 55 acids.

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