

UNITED STATES PATENT OFFICE

2,028,482

SULPHUR DISPERSION

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No Drawing. Application July 3, 1933,
Serial No. 679,093

1 Claim. (Cl. 252-6)

This invention relates to the dispersion of finely divided sulphur in an aqueous medium and generally comprises the use of a dispersing agent of the structure obtained by condensing a naphthalene sulphonic acid, or a homologue or derivative thereof, with formaldehyde or its equivalent, a process and a product thereof, all as hereinafter more fully described and claimed.

Commercial aqueous dispersions of finely divided sulphur are generally made with the aid of protective colloids such as soaps or proteins. The dispersions may be produced either by precipitating sulphur, as by the interaction of hydrogen sulphide and sulphur dioxide, in the presence of an aqueous solution of the protective colloid or by extensive grinding of an ordinary form of elementary sulphur in a water-colloid environment. The former method yields the most finely divided and hence most satisfactory products, but the procedure is very expensive. Furthermore, dispersions prepared according to either procedure are objectionable because the sulphur constituent generally has an undesirable tendency to settle on standing to form hard caked precipitates which are difficult to break up and redisperse, and because the proportion of protective colloid (5-20% of the weight of the dispersed sulphur) which is usually required to yield the most satisfactory results is so large as to alter adversely the physical and chemical properties of the dispersed sulphur itself. Dispersions of sulphur prepared with the aid of the protective colloids formerly employed are also objectionable for some purposes because they are generally flocculated or precipitated by acids or heavy metal ions. This undesirable property is believed to be due to a chemical reaction which occurs between the protective colloid and the flocculating or precipitating agent, e. g., the coagulation of a protein or the decomposition of a soap to form an insoluble fatty acid or heavy metal salt.

Objects of this invention are to provide aqueous dispersions of sulphur which are freer from objectionable non-sulphur constituents, are substantially stable i. e. have less tendency to settle and form hard caked precipitates which are difficult to break up and redisperse, and are less affected by acids or heavy metal ions than materials which have existed previously. Another object is to provide a simple means for preparing directly from any of the usual inexpensive commercial forms of elementary sulphur aqueous dispersions which are comparable in quality with materials which could be prepared heretofore only with the aid of sulphur precipitation proc-

esses. Other objects and advantages of the invention will become apparent with its more detailed description.

I have discovered that aqueous suspensions of finely divided or colloidal sulphur of improved properties may be produced with the aid of one or more members of the class of aromatic compounds of the structure obtained by condensing sulphonic acids of naphthalene, its homologues, or derivatives with formaldehyde or its equivalent. These compounds may be looked upon as derivatives of polynaphthyl alkyls or their homologues and may be expressed by the general graphical formula $(A-R-A')SO_2M$ in which A and A' designate two or more aromatic groups—which may or may not be alike; which contain naphthalene rings joined to an aliphatic nucleus R which may consist of a single alkyl group or a plurality of alkyl groups associated in straight chain or branched chain formation; and in which SO_2M designates at least one solubilizing group such as the free sulphonic acid group or a sulphonic acid group in combination with a soluble salt-forming radical. The members of the class may be synthesized either by direct sulphonation of a hydrocarbon or a derivative thereof which possesses the necessary configuration of at least two naphthalene rings joined to an aliphatic nucleus, or, as is usually more convenient and commercially practical, by causing a naphthalene sulphonic acid or a homologue or derivative thereof to react with formaldehyde or its equivalent, preferably in the ratio of approximately two moles of sulphonic acid for each mol of aldehyde. The member of the family which I prefer to employ because it is cheap and very effective for present purposes may be obtained by condensing betanaphthalene sulphonic acid with formaldehyde.

The condensed and polymerized product may be prepared as follows: To 100 parts of concentrated sulphuric acid (specific gravity 1.84) contained in a suitable sulphonator and maintained at 160° C. are added slowly with stirring 100 parts of refined naphthalene. After all of the naphthalene has been introduced (this operation generally requires about one hour), the mass is stirred at 160° C. for four hours longer or until a test shows that substantially none of the naphthalene remains unsulphonated. The sulphonation mixture is then cooled to about 100° C. and diluted with 44 parts of water to prevent solidification on subsequent cooling. The diluted material is further cooled to 80° C. at which temperature 12 parts of a 40% aqueous solution of formaldehyde are added. This mixture is then

stirred for three hours longer at 80° C.; but at the end of each successive hour there are added 12 parts more of formaldehyde solution, making a total at the end of the three hours of four portions or 48 parts in all. After all the formaldehyde has been added, the temperature is progressively raised over a period of one hour to 95-100° C. where it is maintained for 18 hours while the mass is constantly stirred. Soon after the temperature has been raised to 95-100° C., it is found that substantially none of the aldehyde remains unconsumed in the condensation reaction. During the later stages of the 18-hour heating period, the mixture progressively thickens until at the end it generally reaches the consistency of thick molasses. If this thickening becomes so great, however, as to prevent proper stirring, a small quantity of water may be added to keep the material liquid. After the heating is completed, the mixture is cooled, neutralized with a suitable alkali, e. g. sodium hydroxide, and, if desired, dried. It is then ready for use.

A somewhat purer and better product can be obtained by diluting the viscous reaction mass with about three times its volume of water (the amount is not important so long as it is sufficient to permit convenient handling in the subsequent filtering operation), and neutralizing with lime. For the latter purpose I generally use an aqueous paste or suspension of hydrated or slaked lime. The neutralized slurry is filtered hot to remove the calcium sulphate precipitate which forms from the interaction of the lime and sulphuric acid unconsumed in the sulphonation reaction; and to the filtrate is added the requisite amount of sodium carbonate quantitatively to convert the calcium salt of the desired sulphonic acid into its sodium salt. The resulting calcium carbonate precipitate may then be removed by filtration and the filtrate which contains the desired ingredient evaporated to dryness according to any of the well known drying procedures.

The sulphonation of the naphthalene may be conducted in a cast iron vessel; but the reaction with formaldehyde is preferably carried out in enameled or lead-lined apparatus.

A cheap grade of crude naphthalene may be employed in the foregoing detailed procedure without sacrifice of desirable qualities. The substitution of an alkylated naphthalene, e. g. methyl naphthalene or an ethyl naphthalene, for naphthalene itself results in a product which is particularly effective for present purposes. Such alkylated products, however, which are especially effective for use in the broader aspects of this invention, may be objectionable for some purposes because, due to their tendency to reduce the surface tension of water, they promote the formation of foam in the sulphur dispersion. Materials made from naphthalene sulphonic acids which are free from substituting alkyl groups have substantially no tendency to reduce the surface tension of water; and for this reason sulphur dispersions prepared with them do not have the undesirable tendency to form foam possessed by aqueous dispersions of sulphur prepared with the aid of prior agents which, unlike present materials, generally rely for their effectiveness on their ability to reduce the surface tension of water. The product obtained as described above by the reaction of naphthalene sulphonic acid with formaldehyde is specifically recommended for use in a preferred form of this invention where the tendency to produce foam is objectionable.

In the chemical reaction which occurs between

a sulphonic acid of the naphthalene series and formaldehyde or its equivalent, it is my theory that the initial condensation reaction is followed by a progressive polymerization of the resulting condensed material, and that a certain optimum molecular weight is necessary to yield the best results for present purposes.

Whereas I generally use the sulphonic acids of the herein defined class in the form of their sodium salts, any water-soluble salt or derivative, or even the free acid, may be employed. Salts of monovalent metals, particularly the alkali metals, are preferable, however, to salts of polyvalent metals.

In the practice of my invention aqueous dispersions of finely divided sulphur may be produced according to any of the general manipulative procedures formerly employed. The sulphur may be precipitated, as by the interaction of hydrogen sulphide and sulphur dioxide, in the presence of an aqueous solution of one or more of the herein described agents; or an ordinary form of elementary sulphur, e. g. flowers of sulphur, may be made into a paste with a solution of one or more of the described agents and the wet mixture ground in a ball or colloid mill, or any other suitable form of wet grinding device, to the desired degree of fineness. The former method yields products which are superior in quality to anything known to me which has been prepared heretofore; and the latter method yields dispersions which, so far as I am aware, are better than any which can be made by wet grinding procedures without the aid of this invention and comparable with those formerly prepared by precipitation reactions. It is sometimes desirable to combine the dispersing agent with finely divided sulphur in the dry state and then merely to stir the dry mixture into water. In that case also, my invention affords advantageous results. Such dry mixtures, however, do not yield, when stirred into water, suspended particles of sulphur existing in as finely divided condition as it is possible to obtain by a wet grinding or precipitation procedure.

I have found that, in general, a quantity of dispersing agent equal to 2-5% of the weight of the sulphur to be dispersed yields very satisfactory results. The precise quantity adapted to yield the best results in any given instance depends on the prevailing conditions—in particular, on the concentration of the dispersion, the condition of the sulphur, and the member of the herein described class of dispersing agents which is chosen; but the minimum quantity of agent required to yield the optimum dispersing effect under any given set of conditions may be easily ascertained by trial. It may be stated in general that 4% of material made according to the detailed example given above will afford the best results.

Aqueous dispersions of sulphur prepared with the aid of this invention are substantially stable i. e. they generally display less tendency to settle and produce hard caked precipitates which are difficult to break up and redisperse than like suspensions made according to other methods. This forms one of the principal advantages of the present invention. Similarly, examination under the microscope of dispersions prepared hereunder shows that the particles are less aggregated and engaged in more active Brownian motion than sulphur particles of the same size derived from suspensions of different origin. Furthermore, inasmuch as my dispersing agents are not generally precipitated or destroyed by acids or heavy metal

ions, the addition of these reagents to aqueous dispersions prepared with the aid of this invention generally produces no marked flocculation or precipitation of the suspended particles. This is in contradistinction to the behavior of sulphur suspensions formerly prepared, and makes the process and product of this invention particularly valuable for use in acid environments or in the presence of heavy metal ions normally coagulative of colloidally dispersed material.

I am aware that certain synthetic tanning agents, which are obtained by the condensation of formaldehyde with any one of a large number of aromatic or organic compounds, have been suggested to assist the dispersion of finely divided inorganic materials in water. These synthetic tanning materials are as a class, however, ineffective for my purposes. My discovery is therefore limited to, and resides in, the use of dispersing agents having the structures of the products obtained by condensing formaldehyde or its equivalent with sulphonic acids chosen from the naph-

thalene series; and, as previously stated, I prefer to employ materials which have been subjected to an optimum degree of polymerization.

It should be understood that the present disclosure is for the purpose of illustration only and that this invention includes all modifications and equivalents which fall within the scope of the appended claim.

I claim:

As a new composition of matter, an aqueous dispersion of sulphur which contains a soluble compound comprising the product obtained by condensing an aldehyde with a sulphonic acid of the naphthalene series, said composition obtained by grinding the sulphur in an aqueous solution of the compound and being a stable fluid substantially devoid of precipitated sulphur such as would produce caking, and showing a more active Brownian movement than sulphur particles of the same size in aqueous solutions of other protective colloids.

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