

ALIEN PROPERTY CUSTODIAN

PROCESS FOR PREPARING SULPHUR DYES SOLUBLE IN WATER

Filippo Bovini, Milan, Italy; vested in the Alien Property Custodian

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It is known since a long time, that many sulphur dyes obtained by precipitating the respective molten masses with acids or air, show a tendency to dissolve under the action of sulphite or sodium bisulphite.

The compounds obtained by salting or evaporating sulphite or bisulphite solutions show a certain solubility in water and they do not reprecipitate from their diluted aqueous solutions under the action of acids or by oxidation with air.

Laval's cachou was among the first sulphur dyes treated according to the above procedure, followed later on by other sulphur browns obtained by the combination of a variety of intermediates with sulphur or polysulphides.

The constitution of these soluble compounds, which has been differently explained, is insignificant as far as the practical purpose of this invention is concerned, namely dyeing and printing textile fibres, leather dyeing and similar operations.

As a matter of fact, these compounds have been experienced in the respective fields of application, especially in cotton and wool dyeing, but in spite of certain developments directed to improve their tinctorial properties, results have shown unsatisfactory.

When dyed on wool in acid solution they show very scarce tinctorial properties, and when applied to cotton they show even in the presence of sodium sulphide or of other reducing agents less affinity and much lower covering power than the sulphur dyes they derive from.

In leather dyeing the properties of these compounds appear to be somewhat better, but here too no remarkable progress has even been reached.

Therefore, although the discovery of these soluble compounds obtained from brown sulphur dyes by treatment with sulphite or bisulphite is far behind us, they have been completely abandoned.

One cause of the lack of success is certainly due to the unsatisfactory processes proposed for their preparation.

In fact, when preparing sulphur browns according to the patents covering the different processes, it is found that many dyestuffs do not dissolve at all and others only partially and, in any case, it is then difficult, and sometimes impossible, to separate products in powder being completely soluble in water, of valuable tinctorial properties and suitable for practical application.

It may be said, therefore, that no reference is found in literature about a process for the manu-

facture of soluble sulphur browns in form meeting trade requirements.

I have now found that it is possible to obtain compounds completely soluble in water in form of a highly concentrated fine powder having excellent tinctorial properties and the fastness required by treating orange, brown or olive sulphur dyes with sodium bisulphite solutions.

Heat treatment is preferred, either of the finished dyestuff or of the material during an intermediate working step, namely, treating (a) the raw powder obtained by melting various intermediates with sulphur; (b) the paste obtained after precipitating the above raw powder by acid or air from the solution in sulphide; (c) the paste obtained by precipitating, at various temperatures the aqueous solutions of melting products by acid or air, on certain intermediates by sulphides or polysulphides, or the bisulphitation products by acids or salt, according to the examples stated above.

The compounds obtained are of different solubility and more or less sensible to the action of salts and to room pH, according to their nature. Many of them are insoluble or almost insoluble in the bisulphitic room in which they are formed, while they are readily soluble in water after drying and at a suitable degree of dilution.

Also the stability of these compounds to the hydrolytic action of water varies according to the nature of the product, to the temperature, and to the action being on free acid or on sodium salts.

This process is of general character and there are few sulphur browns which do not give good results by this treatment. It can be applied to sulphur browns derivated from intermediates of various nature obtainable by different methods of sulphuration, as it appears from the examples given hereafter.

The soluble compounds in question are used in dyeing in the presence of sodium sulphide, hydro-sulphide or other suitable reducing agents, and they generally possess a good tinctorial property and a fair affinity also in cotton dyeing. But in view of their affinity, covering power and fastness they are particularly suitable for dyeing regenerated cellulose fibres, casein wool, leather, and for Vigoureux-printing on a large variety of fibres.

Examples 1.—The melting mass of Bright Sulphur Orange R (Schultz Tab. VII 1063) is dissolved in a solution of sodium sulphide and reprecipitated by acidification. The paste obtained is kneaded with the double weight of sodium bi-

sulphite in solution of 35° Bé. heated up to 90° C. and maintained at this temperature during about 2 hours. It is then diluted, allowed to cool and filtered. The precipitate is mixed with small amounts of sodium carbonate and dried.

The dry powder thus obtained is completely soluble in water and in the presence of reducing agents it is suitable for dyeing, cotton, viscose, casein woll (Lanital) and leather in bright orange-brown shades of excellent fastness.

Examples 2.—The raw mass obtained by melting *m*-toluylene-diamine with polysulphides is dissolved in hot water, filtered and precipitated by acids in the ordinary way. The paste thus obtained is thoroughly mixed with a double amount by weight of bisulphite in solution of 35° Bé, and then heated up to 90° C. and maintained at this temperature for an hour. The mass is then diluted with hot water in such a way that the product passes entirely in solution. It is filtered slightly salted and the dyestuff is precipitated by hydrogen chloride. Small amounts of sodium carbonate are added to the filtered paste and the product is dried in the usual way.

The powder thus obtained dissolves completely in water and in the presence of sulphur, hydrosulphite, etc. It dyes cotton, viscose, casein woll (Lanital) and leather, in yellowish cachou shades of excellent fastness.

Examples 3.—Sulphur Brown 6 R (ACNA) in form of powder is kneaded with a fourfold amount by weight of bisulphite in solution of 35 Bé. diluted with water and slowly heated up to 90°C. The material is then filtered, salted and completely precipitated by hydrogen chloride. It is filtered and the paste obtained is dried with a small amount of sodium carbonate.

The dry powder thus obtained is completely soluble in water and in the presence of sulphur, hydrosulphite, etc. it dyes cotton, viscose, casein woll (Lanital) and leather in brown-red shades.

Examples 4.—The dry dyestuff obtained by melting 2-4-dinitroaniline and polysulphides is thoroughly mixed with an eightfold amount by weight of sodium bisulphite solution of 35° Bé, heated up to 60°C and diluted with an equal amount of water. It is filtered, salted, and hydrogen chloride is added until the precipitation is completed. The paste obtained by filtration is mixed with small amounts of sodium carbonate and dried.

The dry dyestuff powder is entirely soluble in water and in the presence of sulphur, hydrosulphite or other suitable reducing agents it dyes cotton, viscose, casein woll (Lanital) and leather in brown-black shades of excellent fastness.

Examples 5.—The raw melting mass of Green Sulpholive B (ACNA) in finely pulverized form is mixed with a tenfold amount by weight of sodium bisulphite in solution of 35° Bé, heated up to 95°C and maintained at this temperature until the product is completely dissolved. It is diluted, filtered and salted. It is allowed to cool at room temperature and precipitated by the necessary amount of hydrogen chloride. It is filtered and the paste thus obtained is dried after an addition of small amounts of sodium carbonate.

The powder of this dyestuff is completely soluble in water, and in the presence of sulphur, hydrosulphite or other reducing agents it dyes cotton, viscose, casein woll (Lanital) and leather in green-olive shades of good fastness.

FILIPPO BOVINI.