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CUPROUS COMPLEXES

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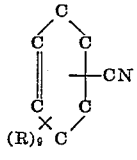
This invention relates to novel cuprous complexes. More particularly, this invention relates to novel, stable, cyclohexenecarbonitrile cuprous complexes useful in aiding the dyeing of acrylonitrile fibers.

It is known in the textile field that synthetic fibers composed of acrylonitrile interpolymers are extremely difficult to dye. To overcome this difficulty, a copper dyeing method was proposed wherein dyeing occurred in the presence of cuprous ions. Satisfactory dyeing results are obtained using the above described process; however, there are some characteristics of this process which make it less desirable when used in large scale dyeing. When the cuprous ion is produced in the dye bath by the reaction of copper compounds, such as copper sulfate, and reducing agents, several deficiencies arise. These deficiencies center around the reduction of the cupric ion to to the active cuprous ion. If the rate of reduction is not carefully controlled, two undesirable occurrences may result. Initially, if the cupric ion is not fully reduced, the chemicals in the bath will be unsatisfactory for use in the dyeing process. On the other hand, if the cupric ion is over-reduced, metallic copper may be present in the bath which will impair both light stability and the color shade of the fiber. In addition, the above-described problems make the dyeing formulations extremely difficult to reproduce. It is the combination of these problems which have discouraged the use of the cuprous-ion technique. There has therefore been a long felt need in the art for a stable cuprous-ion complex which could be added directly to the dyebath without going through the reduction process.

I have discovered a class of novel, inorganic acid salts of cuprous complexes of cyclohexenecarbonitrile which are stable and which can be used to provide outstanding results in the cuprous-ion dyeing technique. A distinct advantage of the compounds of this invention pertains to the fact that not only are the cuprous complexes of cyclohexene-carbonitrile a dyeing aid in acid dyes but also in the dyeing process, the cyclohexenecarbonitrile molecules act as dye carriers. Thus very deep color shades of the dyed fabric can be obtained in the use of the compounds of this invention without the addition of conventional dye carriers.

The cyclohexenecarbonitrile portion of these complexes can be represented by the general formula:



wherein each R, individually, represents a hydrogen atom or an alkyl radical, preferably containing from 1 to 6 carbon atoms.

The cyclohexenecarbonitriles which are used to prepare the novel cuprous complexes of this invention include, for example: 3-cyclohexenecarbonitrile, 2-cyclohexenecarbonitrile, 1-cyclohexenecarbonitrile, 2-methyl-3-cyclohexenecarbonitrile, 3-ethyl-3-cyclohexenecarbonitrile, 5-n-hexyl-3-cyclohexene-carbonitrile, 2-isopropopyl-2-cyclohexenecarbonitrile, 5-ethyl-2-cyclohexenecarbonitrile, 4-n-hexyl-2-cyclohexenecarbonitrile, 3-isopropyl-1-cyclohexenecarbonitrile, 5-n-hexyl-1-cyclohexene-carbonitrile, and the like.

The cuprous salts which are preferably used in the production of the cuprous complexes of this invention include the cuprous salts such as, for example, cuprous chloride, cuprous bromide, cuprous iodide, cuprous nitrate, cuprous sulfate, cuprous phosphate, and the like.

The novel cuprous complexes of cyclohexenecarbonitrile can be readily produced by reacting the cuprous salts such as, for example, cuprous chloride, with a cyclohexenecarbonitrile such as, for example, 3-cyclohexenecarbonitrile at a temperature of from about 20° C. to about 100° C. for a period of time sufficient for the cuprous complex to form and dissolve in the reactant solution. The reaction can be conducted in an inert organic reaction medium which has a function of a solvent in the event that the cyclohexenecarbonitrile starting material is a solid at room temperature. The time of reaction can range from a few minutes to as long as 24 hours depending on the reaction temperature and the specific reactants used. In general, when the cuprous salts are added to the cyclohexene-carbonitrile to produce the products of this invention, the resulting reaction is exothermic. The temperature is controlled and preferably maintained in the range of from about 40° C. to about 80° C. After the initial exothermic reaction has run its course, additional heat can be applied to maintain the temperature and complete the reaction more rapidly.

In producing the novel cuprous complexes of cyclohexenecarbonitrile the cyclohexenecarbonitrile is preferably employed in mole ratios greater than the equivalent amount of cuprous salt present. The preferred range is from about a 1:1 to 1:4 mole ratio of cuprous salts to cyclohexenecarbonitrile. Higher or lower ratios are operable; however a high excess of cyclohexenecarbonitrile is not economically feasible and lower ratios do not make full use of the cuprous salts charged.

In producing the novel cuprous complexes of this invention, it is desirable, although not necessary, to conduct the reaction in an atmosphere of an inert gas free of elemental oxygen, such as an atmosphere of nitrogen, carbon dioxide, helium, and the like. The inert atmosphere aids in decreasing the possible air oxidation of the cuprous salts to the undesirable cupric salts although the cuprous complexes of cyclohexenecarbonitrile can be produced in the presence of air.

Among the cuprous complexes of this invention which can be produced by the above described process are, for example: complex of cuprous chloride and 3-cyclohexenecarbonitrile, complex of cuprous chloride and 2-cyclohexene-carbonitrile, complex of cuprous chloride and 5-n-hexyl-3-cyclohexenecarbonitrile, complex of cuprous chloride and 2-isopropyl-3-cyclohexenecarbonitrile, complex of cuprous bromide and 3-cyclohexenecarbonitrile, complex of cuprous bromide and 5-n-hexyl-1-cyclohexenecarbonitrile, complex of cuprous nitrate and 2-cyclohexenecarbonitrile, complex of cuprous nitrate and 1-cyclohexenecarbonitrile, and the like.

The cuprous complexes of the invention can be recovered from their reaction mixtures in high purity by cooling the reaction mixture to precipitate the cuprous complex and isolation by conventional filtration procedure. If the cuprous complex reaction product does not crystallize on cooling, the reaction product can be precipitated by the addition of an organic non-solvent such as acetone, ethyl ether, ethyl acetate, dioxane, and the like. If additional purification of the copper com-

plexes is desired, conventional recrystallization procedures can be used.

The following examples are illustrative:

Example 1

Cuprous chloride (10 grams) was added portionwise with agitation to 54 grams of 3-cyclohexenecarbonitrile in a nitrogen atmosphere. The reaction was exothermic, raising the temperature from about 20° C. to 35° C. during the addition. After completion of the addition of the cuprous chloride, the reaction mixture was kept at 75° C. for 4 hours. The reaction mixture was filtered warm and stored overnight in a refrigerator at a temperature of approximately 10° C. where the reaction mixture crystallized to a solid mass. The reaction mixture was warmed to room temperature and the solid was filtered, the filter cake was recrystallized from acetone, dried at room temperature and analyzed to be the desired cuprous chloride complex of 3-cyclohexenecarbonitrile. It melted at 72–74° C.

The infrared spectrum and analytical data confirmed the structure as $2C_6H_9CN+CuCl$.

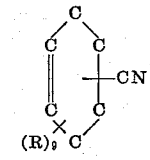
In an analogous manner, 5-n-hexyl-3-cyclohexene-carbonitrile is reacted with cuprous nitrate to obtain the corresponding cuprous nitrate complex of 5-n-hexyl-3-cyclohexenecarobnitrile. Additionally, 2-cyclohexenecarbonitrile is reacted with cuprous sulfate to obtain the corresponding cuprous sulfate complex of 2-cyclohexenecarbonitrile.

Example 2

A 5 gram sample of scoured and dried knitted tubing of continuous yarns composed of a terpolymer of acrylonitrile, vinyl chloride and vinylidene chloride [in a ratio, respectively, of 70:20:10] was added to a 200 milliliter total volume aqueous dyebath containing 1 percent by weight of the yarn of Pergegal OK (a cationic condensation product of ethylene oxide and an organic amine marketed by General Aniline and Film Corporation), 2 percent by weight of the yarn of concentrated sulfuric acid, 3 percent by weight of the yarn of Xylene Milling Blue G.L. (Acid Blue 102–50315) and 3.0 percent by weight of the yarn of the cuprous chloride complex of 3-cyclohexenecarbonitrile. The cuprous chloride complex of 3-cyclohexenecarbonitrile was added as a mixture of 5 parts by weight of acetonitrile to 1 part by weight of cuprous chloride complex of 3-cyclohexenecarbonitrile. The bath temperature was raised to boiling in about 20 minutes and held for 90 minutes at the boiling temperature. The dyed fabric was then raised, scoured, rinsed, hydroextracted and dried at 130° C. for 10 minutes. After drying, the dyed fabric had a final K/S* value of 12.9. The common Fade-O-Meter test indicated a light fastness rating of the dyed fabric of 40 hours.

What is claimed is:

1. The cuprous complex produced by the reaction of a cuprous salt of an inorganic mineral acid with a cyclohexene-carbonitrile of the formula:



wherein each R, individually is selected from the group consisting of hydrogen and the alkyl radicals of from 1 to 6 carbon atoms, at a temperature of from about 20° C. to about 100° C.

2. The cuprous complex produced by the reaction of cuprous chloride with 3-cyclohexenecarbonitrile at a temperature of from about 20° C. to about 100° C.

3. The cuprous complex produced by the reaction of cuprous nitrate with 5-n-hexyl-3-cyclohexenecarbonitrile at a temperature of from about 20° C. to about 100° C.

4. The cuprous complex produced by the reaction of cuprous sulfate with 2-cyclohexenecarbonitrile at a temperature of from about 20° C. to about 100° C.

No references cited.

*The amount of dye on fiber or the depth of color are approximately proportional to the K/S value which is a measure of the light reflected from the dyed sample. The larger the K/S value, the deeper the shade; and a K/S value of 20 is approximately twice as deep as a K/S value of 10. The determination of the K/S values is set forth in an article by D. B. Judd, Color in Business, Science and Industry, 1952, pp. 314–342.