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NAPHTHOYL LEUCO METHYLENE BLUE

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This invention relates to the substantially light-stable leucomethylene blue derivative 10-naphthoyl-3,7-bis-(dimethylamino) phenothiazine, having the structure

where R is taken from the group consisting of 1-naphthoyl and 2-naphthoyl.

The known leucomethylene blue compound 10-benzovl-3,7-bis(dimethylamino)phenothiazine has been used as a color reactant in connection with manifold sheets such 25 as those described in the United States Patent No. 2,646,367, which issued on the application of Chester Davis and Ned A. Thacker on July 21, 1953. In that patent, there is disclosed a manifold sheet having a colorless transfer coating on one side, the coating being made of wax and an oil having dissolved in it the colorless color reactant crystal violet lactone, which is 3,3-bis-(p-dimethylaminophenyl)-6-dimethylaminophthalide, and the beforementioned benzoyl leucomethylene blue. If such a manifold sheet is placed with the transfer coating 35 in contact with the surface of a copy sheet sensitized with particles of attapulgite, halloysite, or equivalent acid claylike material, and an impression is made by printing or writing on the top side of the manifold sheet, the color reactants will be transferred with the oil onto the sensitized surface of the copy sheet. The crystal violet lactone will immediately turn dark blue when coming into contact with the sensitizing clay-like material, thus manifesting whatever was printed or written on the top sheet. After prolonged exposure to light, this dark blue color will fade, but the benzoyl leucomethylene blue will be developing a blue-green color, so that the printed or written matter will not be lost.

The benzoyl leucomethylene blue has one characteristic in its disfavor, and that is that it slowly decomposes to the blue-green color on exposure to light, which means that, if the transfer coating is exposed to light for a long time, it turns to an undesirable blue-green color.

Therefore, it is the object of this invention to provide more light-stable naphthoylated derivatives of leucomethylene blue.

The manufacture of 10-(2-naphthoyl)-3,7-bis (dimethylamino)phenothiazine may be started with the commercially available zinc chloride double salt of leucomethylene blue, having the structure

$$\begin{bmatrix} \operatorname{HCl} \cdot (\operatorname{CH}_3)_2 \operatorname{N} & \operatorname{N} \cdot (\operatorname{CH}_3)_2 \cdot \operatorname{HCl} \\ \operatorname{N} & \operatorname{HCl}_2 \end{bmatrix} \cdot \operatorname{ZnCl}_2$$

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To 35 grams (0.0706 mole) of the zinc chloride double salt of leucomethylene blue is added 97 grams (1.25 moles) of pyridine in a three-necked, round-bottom flask fitted with a mechanical stirrer, a thermometer, and a reflux condenser. To the above mixture is added slowly 25 grams (0.131 mole) of 2-naphthoyl chloride while

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stirring. The reaction mixture is refluxed gently for one hour. The resultant hot reaction mixture then is poured into one liter of cold water and mechanically stirred for one half hour. The brown semi-solid precipitate which forms is washed with water and thereafter stirred with 17.5 grams of sodium hydroxide dissolved in one half liter of water for one half hour. The alkaline solution then is decanted off, and the semi-solid residue is washed with water and extracted with 2.2 liters of hot benzene. The dark benzene solution then is treated with fuller's earth and filtered. The resultant amber filtrate is concentrated to 400 milliliters and precipitated with petroleum ether.

The resulting final product, 10-(2-naphthoyl)-3,7-bis-(dimethylamino)phenothiazine, is a light yellow crystalline material having the following structure:

In making the 1-naphthoyl derivative, 10-(1-naphthoyl)-3,7-bis(dimethylamino)phenothiazine, having the structure

the same process is used as in making the 2-naphthoyl derivative except that 1-naphthoyl chloride is used in place of 2-naphthoyl chloride. The 1-naphthoyl derivative also is a light yellow crystalline material.

The light yellow color is imperceptible in the amount used in thin films on the transfer coatings mentioned, and the material will turn to a blue-green color when in prolonged contact with attapulgite or halloysite.

What is claimed is:
1. 10 - naphthoyl - 3,7 - bis(dimethylamino)phenothiazine, having the structure

in which R is taken from the group consisting of 1-naphthoyl and 2-naphthoyl.

2. The substantially light-stable leucomethylene blue derivative 10 - (2-naphthoyl) - 3,7 - bis(dimethylamino)-phenothiazine, having the following structure:

3. The substantially light-stable leucomethylene blue derivative 10-(1-naphthoyl) - 3,7 - bis(dimethylamino)-phenothiazine, having the following structure:

113,721 Germany _____ Sept. 28, 1900 512,300 Belgium ____ July 15, 1952 725,275 Great Britain _____ Mar. 2, 1955

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