

**A PROCESS FOR THE PREPARATION OF A PIGMENT DYESTUFF**

The invention relates to a modified azo pigment and a new process for its production.

The compound of formula I defined below is described in Example 20 of US patent 3,997,521 and has been found to have the CIELAB values as follows:

$$L^* = 79.51$$

$$a^* = 15.18$$

$$b^* = 86.77$$

$$C^* = 88.09$$

$$H^* = 80.08$$

The CIELAB values were determined with 25.3% by weight of the pigment according to Example 20 of USP 3,997,521 in an alkyd-melamine-formaldehyde resin coating.

The alkyd-melamine-formaldehyde (AMF) resin coating was made up as follows (all in parts by weight):

15 parts of pigment are dispersed with 10 parts of a colorless dispersing agent (Disperbyk 160) 67.78 parts of alkyd-melamine-formaldehyde lacquer, 6.79 parts of xylene and 180 parts of glass pearls (3 mm in size) were ground over 3 hours in a "Red Devil" (a milling process). This is applied preferably with a doctor blade onto white carton paper to a thickness of 0.15 mm and hardened at 120°C for 30 minutes.

The AMF resin comprises:

18.5 parts of xylene

1.44 parts of butyl glycol acetate

10.00 parts of melamine-formaldehyde resin "Maprenol 650" in

8.20 parts of isobutanol.

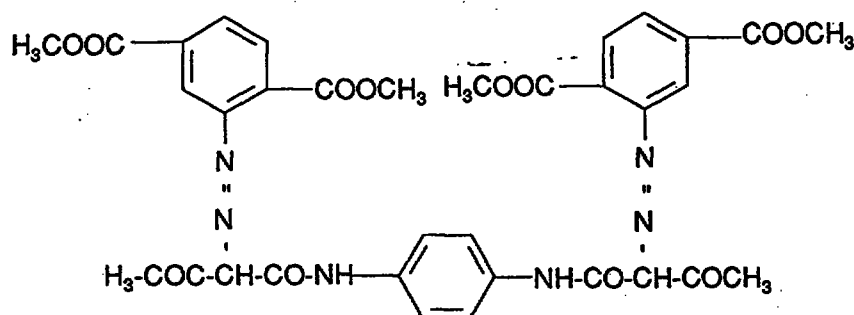
20.00 parts of coco alkyd resin "Alphtalat AC 451N" in 8.56 parts of "Solvesso 100" (a mixture

of aromatic solvents having a boiling point range of 162°C to 177°C).

20.00 parts of coco alkyl "Alphalat AC 451M" dissolved in 13.30 parts of a 50:50 mixture of xylene and Solvesso 150 (a mixture of aromatic solvents having a boiling point range of 187-211°C).

However it has been found to have dispersibility properties that are not optimum and to have a nuance that is also not optimum. These problems are alleviated by preparing a modified pigment according to the invention.

According to the invention there is provided a modified compound of formula I



having the following CIELAB values:

$$L^* = 82.55$$

$$a^* = 11.53$$

$$b^* = 90.49$$

$$C^* = 91.22 \text{ and}$$

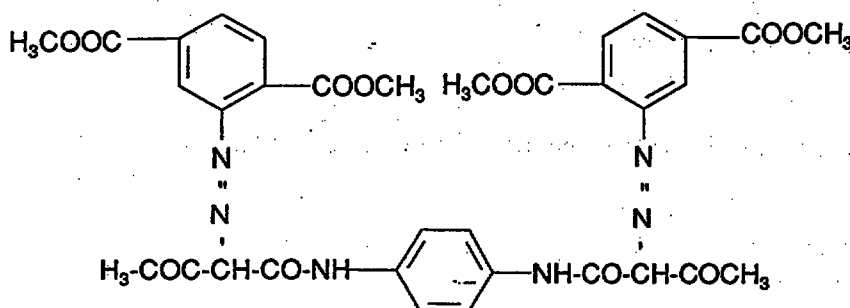
$$H^* = 82.74.$$

The CIELAB values are as defined in J. Soc. Dyers and Colourists Sept. 1976 p. 337 et seq. especially pages 337 and 338.

The CIELAB values were determined with 25.3% by weight of the pigment according to the invention in the above mentioned alkyd-melamine-formaldehyde resin coating.

The CIELAB values given are +/- 1% more preferably +/- 0.5%.

Further according to the invention there is provided a process for preparing a compound of formula I



characterized by

- dissolving 1,4-bis-(acetoacetyl-amino)benzene in an aqueous alkaline hydroxide solution,
- precipitating 1,4-bis(acetoacetyl-amino)benzene to form a suspension preferably by bringing the pH of the solution to pH 6.5 to 7.5, and
- then coupling the product of b) above with a solution of diazotized 2-aminoterephthalic acid dimethyl ester; the molar ratio of diazotized 2-aminoterephthalic acid dimethyl ester to 1,4-bis-(acetoacetyl-amino)benzene being about 2:1 (preferably 2:1).

The resulting pigment may be filtered, washed salt free, with water dried and treated with a higher boiling solvent and then isolated according to conventional methods.

Preferably in the process according to the invention the pigment after reaction is filtered, washed salt free with water, dried and treated with organic solvent, over a period of up to 6

hours, preferably 1 to 5 hours at 80 to 150°C. After the product has been filtered, washed salt free, dried and treated in an organic solvent, it may be further treated by filtration, washing, drying and crushed to form the desired smaller particles.

The pigment made according to the process according to the invention can be applied to polymeric material and has better purity of nuance, has a greener nuance, is more stable to light and has a better stability to heat (especially in polypropylene) and is more easily dispersed in polyolefins than that made according to Example 20 of US Patent 3 997 521.

Preferred polymeric material include solvent-containing and solvent free plastics, e.g. is polyolefin, polyvinylchloride (PVC), polystyrene, acrylic, polyester, alkyd or polyurethane lacquers. Preferred polymeric material and methods for applying the pigment to the material are as described in USP 3,997,521, which is incorporated herein by reference.

Preferably in a process according to the invention the pH is brought to 6.5 to 7.5 by the addition of organic and/or inorganic acid, for example glacial acetic acid and/or hydrochloric acid.

In this Specification, DISPERBYK, RED DEVIL SOLVESSO and HYFLO are trademarks.

The invention will be illustrated by the following example in which all part and percentages are by weight and all temperatures are in degrees C.

#### Example

- a. 104.5 parts of the dimethyl ester of 2-aminoterephthalic acid are stirred into a mixture of 70 parts water, 111.5 parts of glacial acetic acid, 150 parts of 30% hydrochloric acid solution and 0.3 parts of the sodium salt of dinaphthylmethane disulphonic acid.

This mixture is stirred for 4 hours. 100 parts of ice are added to the suspension and the mixture is put in an ice bath to cool it down to 0°.

35.2 parts of sodium nitrite (in the form of 150 parts of an aqueous solution) are then added over 1 hour keeping the temperature between 0° and 5° with the addition of ice, whereby the suspension changes into a clear yellow-brown solution. The excess nitrite is destroyed by using amino sulphonic acid solution. To purify the solution, 5 parts of a commercially available filter earth are added, the mixture is stirred and the filter earth is filtered off and then the residue is washed with a little water.

- b. 93.1 parts of 30% NaOH solution is added to 500 parts water at 10°.

69.0 parts of 1,4-bis-(acetoacetylamino)benzene are then added and the mixture is stirred for 30 minutes after which 5.0 parts of a commercially available filter earth are added. The mixture is then stirred again and the solution is filtered off and the filter earth washed with a little water. In the course of 30 minutes a solution of 400 parts of water, 400 parts of ice, 73.5 parts glacial acetic and then 53.2 parts of 30% NaOH solution is added while stirring.

- c. The diazonium salt solution of part a) above is run into the suspension of part b) above over 2 hours. This is then stirred for a further 2 hours with a slight increase in temperature, is then stirred for 1 hour at 40 to 45°C, is then stirred for a further hour at 65°C and finally

is stirred for a further hour at 80°C. The resulting yellow precipitate is then filtered, washed with cold water to remove any salt and then dried conventionally under vacuum (the remaining amount of water is less than 1%).

- d. 71.6 parts of the resulting pigment is then stirred with 570 parts of dimethylformamide for 2 hours at 150°, then cooled to 80 to 100°C, filtered and washed with a low boiling point alcohol, dried and ground.

The resulting pigment is of formula I defined above and in a lacquer as given above, has the CIELAB values as follows:

$$L^* = 82.55$$

$$a^* = 11.53$$

$$b^* = 90.49$$

$$C^* = 91.22 \text{ and}$$

$$H^* = 82.74$$

The colorimetric differences compared to the compound made according to Example 20 of US Patent 3 997 521 are as follows:

$$DL^* = 3.04$$

$$Da^* = -3.65$$

$$Db^* = 3.72$$

$$DC^* = 3.13$$

$$DH^* = 4.16 \text{ and}$$

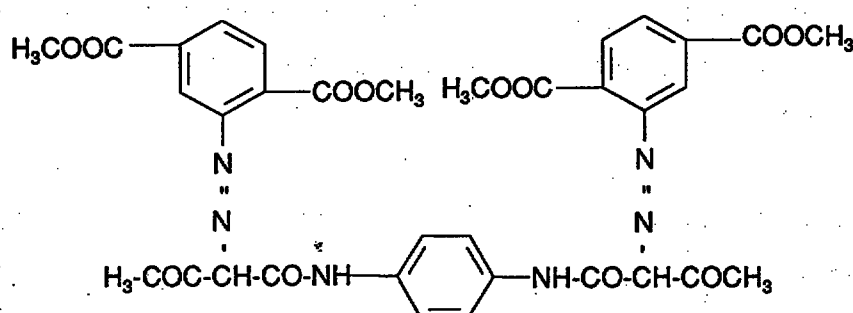
$$DE^* = 6.03. (DE^* \text{ is the total difference in the color change.})$$

The pigment has improved properties and can be used to color solvent-containing and solvent-free plastics material and plastics resins a green-yellow tone. The resultant fastness properties are very good.

The filter earth used is "Hyflo" (a filtering earth) from Mexico.

CLAIMS:

1. A modified compound of formula I



having the following CIELAB values:

$$L^* = 82.55$$

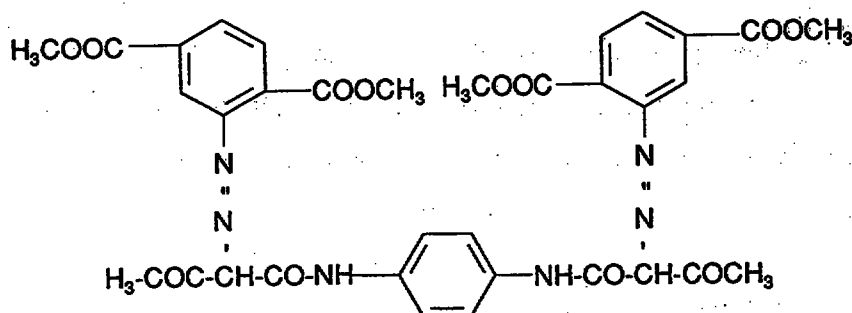
$$a^* = 11.53$$

$$b^* = 90.49$$

$$C^* = 91.22 \text{ and}$$

$$H^* = 82.74.$$

2. A process for preparing a compound of formula I



characterized by



- a) dissolving 1,4-bis-(acetoacetyl amino)benzene in an aqueous alkaline hydroxide solution,  
b) precipitating 1,4-bis(acetoacetyl amino)benzene to form a suspension, and  
c) then coupling the product of b) above with a solution of diazotized 2-aminoterephthalic acid dimethyl ester; the molar ratio of diazotized 2-aminoterephthalic acid dimethyl ester to 1,4-bis(acetoacetyl amino)benzene being about 2:1.
3. A process according to Claim 2 in which the compound is precipitated by bringing the pH of the solution to pH 6.5 to 7.5.
4. A process according to Claim 3 in which the resulting product is treated with a higher boiling point solvent and then isolated.
5. A process according to any one of Claims 2 to 4 in which the resulting pigment of formula I is filtered, washed with water, dried and treated with organic solvent, over a period of up to 6 hours after which it is optionally further treated by filtration, washing, drying and crushed to form the desired smaller particles.
6. Polymeric material to which a pigment according to Claim 1 has been applied.
7. A modified compound of formula I substantially as herein described with reference to the Example.
8. A process according to Claim 2 substantially as herein described with reference to the Example.
9. Polymeric material to which the compound of Claim 7 or the product of the process of Claim 8 has been applied.
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