

SURFACE TREATMENT OF ORGANIC PIGMENTS
FOR PRINTING INK APPLICATIONS

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Abstract: This paper describes some of the advantages of surface treatments, discusses the generally accepted mechanism for how surface treatments act and then shows some examples of surface treatments from the recent U.S. Patent Literature.

Advantages of Surface Treatments

Ink makers who have worked with pigments that are not surface treated have probably experienced difficulties with these pigments. Some of the advantages of surface treatments include the following properties: Easier dispersibility, higher pigment content and/or lower viscosity ink bases and better stability to flocculation.

Surface treatments impart easier dispersibility, which offers several advantages: Pigment dispersions are achieved faster, which allows lower energy costs (fewer passes through the equipment) and/or lower equipment costs (simpler equipment). The resulting dispersions contain fewer agglomerates or grit from dispersing dry pigments into ink bases or pigment presscakes into flushed bases. Also, the resulting dispersions usually show higher strength, higher gloss and higher transparency.

Surface treatments allow manufacture of higher pigment content ink bases; even though these bases contain more pigment, their viscosities will be similar to those of bases made with untreated pigments at the usual pigment contents. Conversely, surface treatments allow manufacture of ink bases with lower viscosity at the usual pigment contents.

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Surface treatments impart better stability and flocculation resistance to pigments. This is particularly important when the pigments are used in fluid inks (gravure and flexographic).

Mechanism of Surface Treatments

Usually in technical papers, examples and results are presented, followed by the proposed hypothesis or mechanism that seems to explain them. Since the subject of surface treatment is not widely known and its mechanism is generally accepted by technical people in the field, it is probably better pedagogically to present the generally accepted mechanism followed by the specific examples.

The organic pigments used in printing inks contain many polar functional groups (Patton, 1973a). Figure 1 shows the molecular structures of the Diarylide Yellows. The simplest Yellow, AAA Yellow, contains chlorine, azo, ketone and amide groups. The more substituted green shade and red shade yellows, AAOY Yellow and AAMX Yellow, also contain these groups. The more heat stable green shade AAOA Yellow contains these groups plus methoxy groups.

The red pigments used in printing inks not only contain polar groups, but also ionic groups, as shown in Figure 2. Lithol Rubine (Red 57) contains carboxylate anion, hydroxyl, azo, sulfonate anion and calcium cation.

The other Rubine, Red 52, contains these groups plus a chlorine group. The chlorine-containing C-amine used to make Red 52 is also used to make a warm red, Red Lake C, which contains chlorine, sulfonate anion, barium cation, azo and hydroxyl groups. Similarly, Barium Lithol Red contains polar and ionic groups.

Molecular structures for the organic blue and black pigments used in printing inks are shown in Figure 3. Copper Phthalocyanine Blue contains a copper cation and several nitrogen groups. Although the structure of Carbon Black is complex, unknown and variable, a simplified graphite structure is shown; occasional ketone, carboxylic acid, etc. groups have been identified.

When the individual pigment molecules containing polar groups are stacked up into pigment crystals, the resulting pigment particles have large surface areas containing polar groups. Figure 4 shows the inverse relationship between

color strength and pigment particle size, as published in the papers of W. Carr of Ciba-Geigy, Ltd. The graph on the right shows that, as the strengths of Phthalo Green and AAOA Yellow are increased, their particle sizes are decreased. Similarly in the left graph, the stronger Lithol Rubine has a smaller particle size. The inverse relationship between particle size (d_m) and surface area (S.A.) is shown in the equation at the bottom left: Pigments with small particle size have large surface areas. Therefore, modern high strength pigments have small particle sizes and large surface areas which contain polar groups.

In contrast, the ink vehicles into which these pigments are dispersed are generally non-polar. Figure 5 shows the molecular structures for some ink resins and oils. Polyindene resins and polycyclopentadiene resins contain no polar groups (Mark, 1966). The rosin ester of pentaerythritol contains polar ester groups, but these are shielded by the rosin polycyclic moieties.

The oils in which these resins are dissolved are similarly non-polar. These oils contain aliphatic hydrocarbons, like tridecane, and cycloaliphatic hydrocarbons, like cyclohexyl heptane (as shown).

The non-polar resins and oils have little affinity for the polar areas of the pigment particles and wet them poorly. This is why it is difficult to disperse high strength pigments with large areas of polarity into non-polar vehicles.

The generally accepted mechanism for surface treatment is illustrated in Figure 6. It is hypothesized that surface treatment acts as an interface or bridge between the polar areas of the pigment surfaces and the non-polar oily vehicles. On the left is shown an idealized pigment particle with various polar groups on its surface in (energetically unfavorable) contact with the oily vehicle. Surface treatment covers the high energy polar surfaces with low energy "oily tails," making this pigment surface more compatible with the vehicle. These "tails" also help keep the pigment particles sterically separated. In addition, these "tails" do not have much mechanical strength and allow easy separation (dispersion) of the pigment particles into the vehicle. In these ways, surface treatments enable the advantages listed earlier to be obtained.

Examples of Surface Treatments

An excellent review of surface treatment was published about 10 years ago (Patton, 1973b). Two Farbwerke Hoechst AG scientists, K. Merkle and H. Schäfer, covered the European patent literature up through about 1970.

To cover the last thirteen years and to emphasize the U.S. Patent literature, the writer worked with the Inmont librarian, Ms. Joanne Freeman. After a couple initially unsuccessful attempts, Ms. Freeman developed an effective strategy for searching via computer the Lockheed "Dialog" data bases for pertinent U.S. patents. Of the several dozen U.S. patents discovered in this search, about a dozen typical, representative examples were selected (along with a couple British patents) to illustrate various types of surface treatment.

Pigments can be surface treated with carboxylic acids and their metal salts, as shown in Figure 7. Perhaps the oldest surface treatment is rosination; Imperial Chemical Industries have a patent on treating Phthalocyanine Blue and other pigments with the calcium salt of rosin (Ambler, 1967). To help visualize better how these treatments can shield the polar surfaces, only one molecule of the surface treating agent will be shown. Sherwin Williams patented the treatment of Alkali Blue with fatty acids like stearic acid (Rees, 1977). With the polar heads of calcium rosin-ate or fatty acid adsorbed on the polar surfaces of the pigments, the non-polar "tails" can project out and effectively shield the polar surfaces from the non-polar vehicle.

Alkyl sulfonate or sulfate salts have been patented, as shown in Figure 8. Dialkyl sulfosuccinates, e.g., Aerosol OT, form Calcium, Barium or Aluminum salts which can be used to treat Lithol Rubine, as claimed by Alexander Hamilton (1971). Similarly, the metal salts of alkyl benzene sulfonates or alkyl sulfates can be used; Toyo Ink have a recent patent on the metal salts of the latter, e.g., Duponol WAQ, for treating Phthalocyanine Blue (Funatsu, 1980). Again, note how the polar groups can be adsorbed on the polar areas, leaving the alkyl "tails" projecting up.

Figure 9 shows alkyl amines or ammonium salts as surface treatments. Kemisk Vaerk Koge have a British patent on treating AAA Yellow, Red Lake C and Phthalocyanine Blue with alkyl propylenediamines (Jensen, 1967); although this type of treatment is excellent with pigments for Publication

Gravure inks, in offset inks it causes problems with emulsification of acidic fountain solution into the inks and with scumming of the lithographic plate (Kaupp, 1978). The cyclohexyl ammonium salt of rosin was patented by Bayer for treating AAA Yellow and other pigments (Wolf, 1972). The alkyl ammonium salt of dodecylbenzene sulfonic acid was claimed by Geigy in a British patent for treating various Diarylide Yellows and Lithol Rubine (Hossack, 1967). Again, note the hydrocarbon tails shielding the polar surfaces.

An alkyldiol and amino alkanol are shown in Figure 10. The alkyndiol shown, Surfynol 104, is claimed for treating nigrosine dyes in a patent application by I.B.M. (Moore, 1981). Henkel have a patent on treating titanium dioxide with vicinal amino alkanols (Linden, 1979).

All of these surface treatments, from rosination to amino alkanols, are relatively simple and inexpensive, but can suffer from a couple disadvantages: they are not specific enough for the polar areas, so too much is needed for adequate treatment; or they may be too soluble in the ink vehicle, so they are easily desorbed from the polar areas, again requiring too much for adequate treatment.

To overcome these disadvantages, some companies have developed more sophisticated, polycyclic surface treatments. The polycyclic "heads" of the molecules are much closer in molecular structure to the polar areas of pigments; consequently, they are much more specific for the polar areas of the pigments and have lower solubility in the ink vehicle. The polycyclic molecules fall into two general categories, colorless and colored.

Examples of colorless polycyclic surface treatments are shown in Figure 11. At the top are shown two Bis(alkylurea) derivatives (Sappok, 1981): although BASF showed these being used with Phthalocyanine Blue, the diphenylmethane moiety is similar in structure to AAA Yellow and the naphthalene moiety is similar in structure to red pigments; this approach also has the advantage of starting with diisocyanates that are not too expensive. At the bottom is shown a rather complex polycyclic patented by Toyo Ink for treating Phthalocyanine Blue (Katsura, 1982). Colorless polycyclics have the principal advantage of being potentially applicable to any color of pigment.

The colored polycyclic surface treatments are alkyl derivatives of pigments. Figure 12 shows two alkyl derivatives

of Yellows. At the top is shown a Bis (alkyl ketimine) derivative of AAA Yellow patented by I.C.I. (Dawson, 1970). At the bottom is shown a Bis (alkyl amide) derivative, in which the phenyl groups of AAA Yellow are replaced by alkyl groups (Mitchell, 1969a). Since both of these molecules have large moieties identical with AAA Yellow, they would be expected to be very effective surface treatments.

Figure 13 shows alkyl derivatives of blue and red pigments. Ciba-Geigy have a recent patent on a dialkylamine derivative of Phthalocyanine Blue, used for treating Phthalocyanine Blue (Barraclough, 1982). I.C.I. patented an alkyl derivative of an Azo Red, used for treating AAMX Yellow and reds. (Mitchell, 1969b). Again, since these molecules have large moieties identical with or similar to the pigments they are used to treat, they would be expected to be very effective surface treatments.

Conclusion

Surface treatments offer several advantages to users of organic pigments in printing inks: easier dispersibility, higher pigment content/lower viscosity ink bases and better stability/flocculation resistance. The generally accepted mechanism involves the surface treatment covering the large polar areas of the pigments with low energy "oily tails"; these "tails" have low mechanical strength for easy dispersion, make the pigment surfaces much more compatible with the oily vehicle and sterically separate the pigment particles. An effective computerized search strategy was developed to find appropriate U.S. patents on surface treatment. Representative examples of surface treatments ranging from relatively simple rosin salts to complex colorless or colored polycyclics are described.

The writer wishes to thank Ms. Joanne Freeman, whose computerized search of the U.S. Patent Literature made this paper possible.

Literature Cited

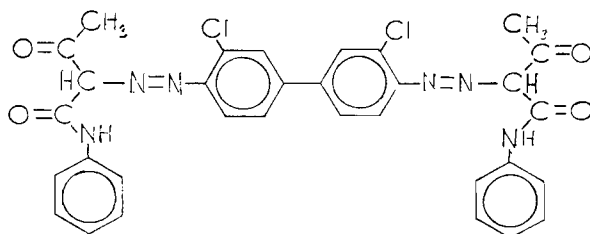
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1977 U.S. Patent 4,032,357 (June 28, 1977).
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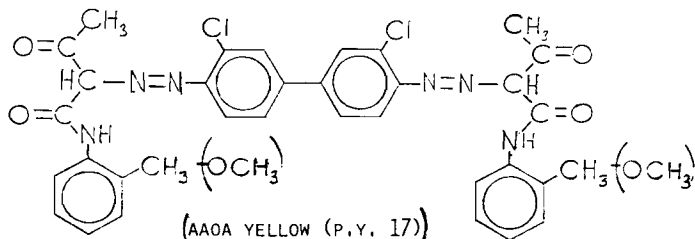
Wolf, K., et al.

1972 U.S. Patent 3,653,936 (April 4, 1972).

FIGURE 1
DIARYLIDE YELLOWS

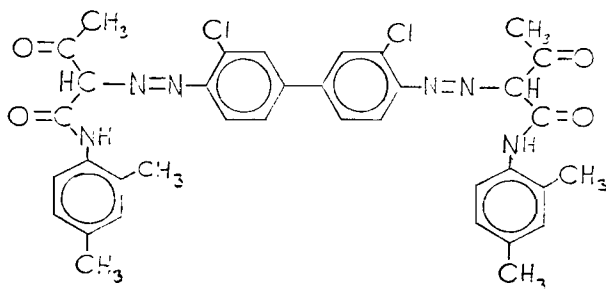


AAA YELLOW (P.Y. 12)



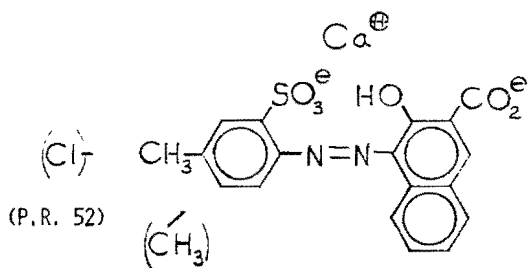
(AAOA YELLOW (P.Y. 17))

AAOT YELLOW (P.Y. 14)

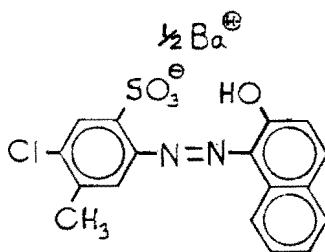


AAMX YELLOW (P.Y. 13)

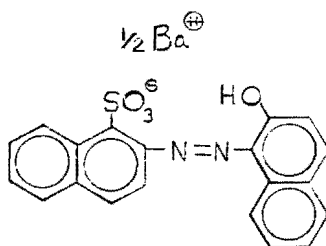
FIGURE 2
REDS



LITHOL RUBINE (P.R. 57)

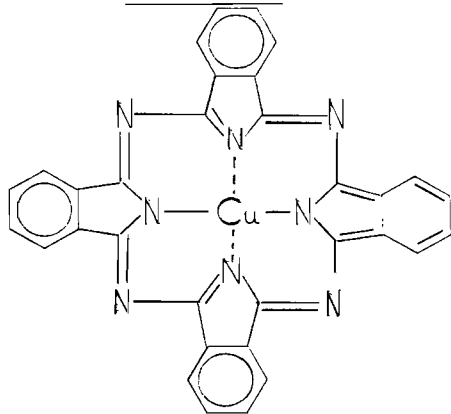


RED LAKE C (P.R. 53)

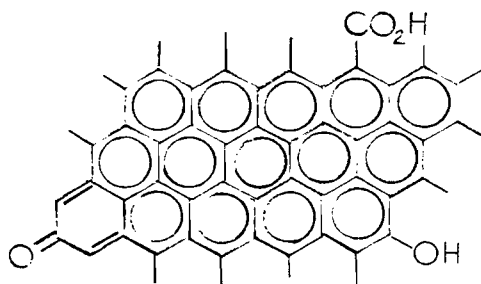


BARIUM LITHOL RED (P.R. 49)

FIGURE 3
BLUE AND BLACK



PHTHALOCYANINE BLUE (P.B. 15)



CARBON BLACK (P.B. 7)

FIGURE 4

STRENGTH vs. PARTICLE SIZE

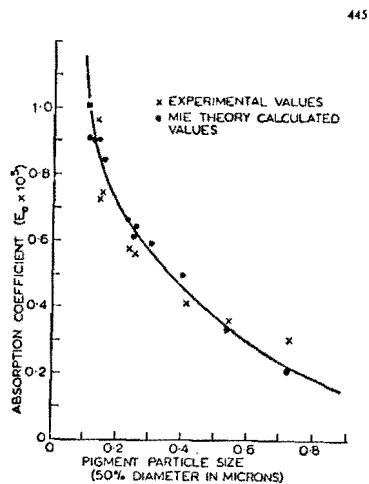


Fig. 2. Colour strength versus pigment dispersion for a calcium 4B toner (Rubine 4B—C.I. Pigment Red 57) in decorative paints (1)

- (1) W. Carr, J. Oil Col. Chem. Assoc., 59, 445 (1976).
 (2) W. Carr, J. Paint Tech., 42, 709 (1970).

$$S.A. = (G/p) \sum W/d_m \propto \frac{1}{d_m}$$

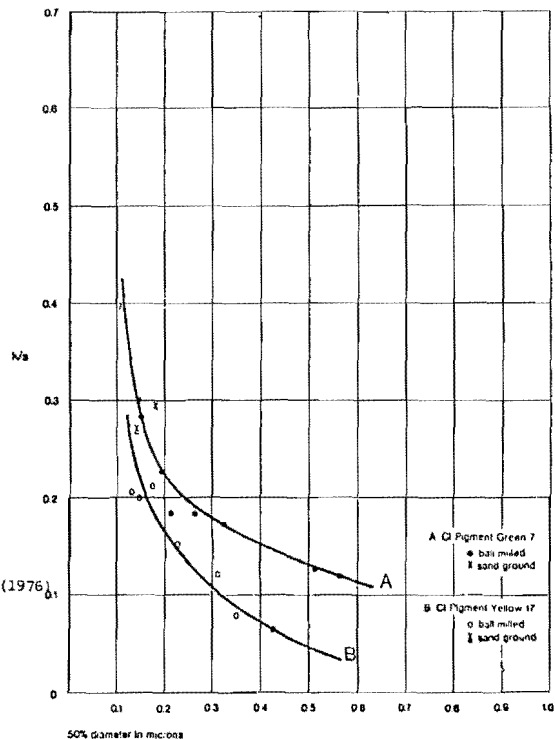
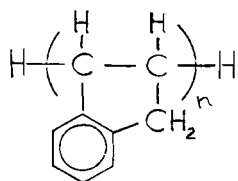


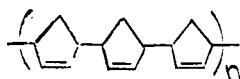
Figure 14—Phthalocyanine green and diarylide yellow paint stainers in 1:75 reductions with titanium dioxide (2)

FIGURE 5
VEHICLES (RESINS AND OILS)

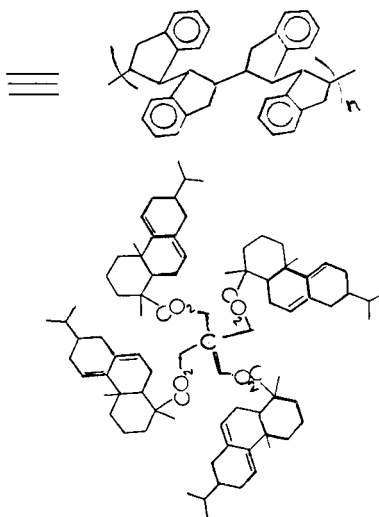
RESINS



POLYINDENE



POLYCYCLOPENTADIENE

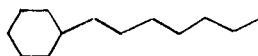


PENTA ERYTHRITOL
ESTER OF ROSIN

OILS



ALIPHATIC

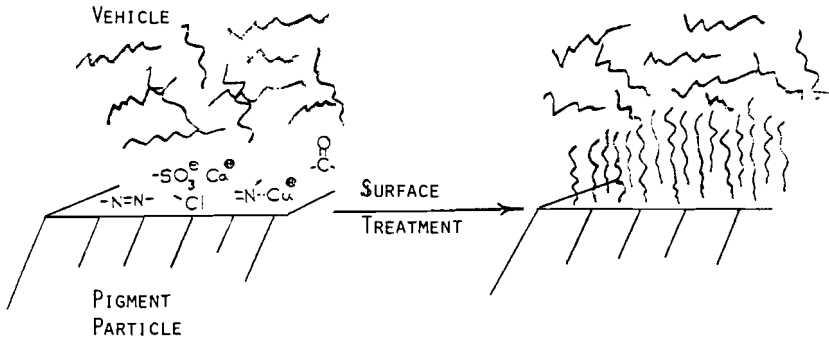


CYCLOALIPHATIC

FIGURE 6

PROPOSED MECHANISM FOR SURFACE TREATMENT

HYPOTHESIS: SURFACE TREATMENT ACTS AS INTERFACE BETWEEN POLAR AREAS OF PIGMENT SURFACES AND OILY VEHICLES.

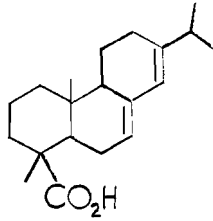


SURFACE TREATMENT:

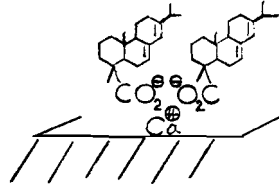
- COVERS HIGH ENERGY POLAR SURFACES WITH LOW ENERGY "OILY TAILS".
- STERICALLY SEPARATES PIGMENT PARTICLES.
- IMPARTS LOW MECHANICAL STRENGTH COATING.

FIGURE 7

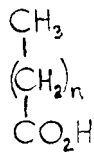
CARBOXYLIC ACIDS AND THEIR METAL SALTS



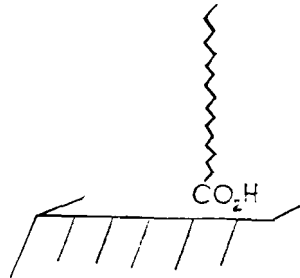
ROSIN
(ABIETIC ACID)



U.S. PAT. 3,296,001
(I.C.I., 1967)



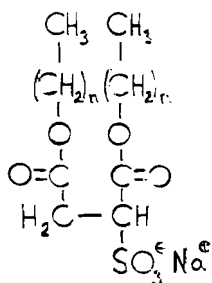
FATTY ACID



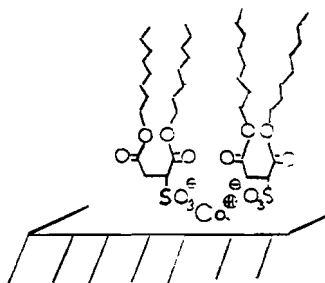
U.S. PAT. 4,032,357
(SHERWIN-WILLIAMS, 1977)

FIGURE 8

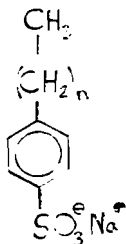
ALKYL SULFONATE OR SULFATE SALTS



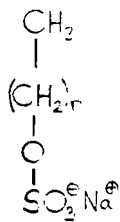
SODIUM DIALKYL
SULFOSUCCINATE



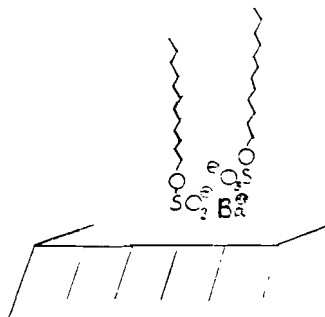
U.S. PAT. 3,582,380
(ALEXANDER HAMILTON, UNASSIGNED, 1971)



SODIUM ALKYL
BENZENE
SULFONATE

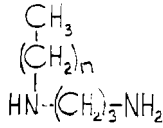


SODIUM
ALKYL
SULFATE

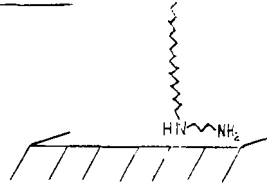


U.S. 4,221,606
(TOYO INK, 1980)

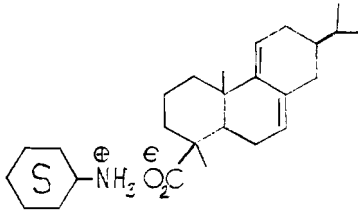
FIGURE 9
ALKYL AMINES OR AMMONIUM SALTS



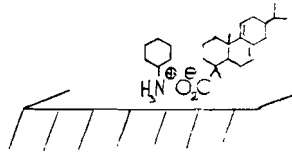
N-ALKYL -
PROPYLENE DIAMINE



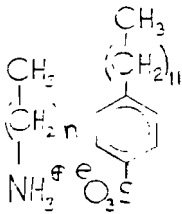
U.K. PAT. 1,080,115
(KVK, 1967)



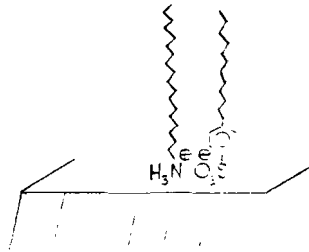
CYCLO HEXYLAMMONIUM
ROSINATE



U.S. PAT. 3,653,936
(BAYER, 1972)



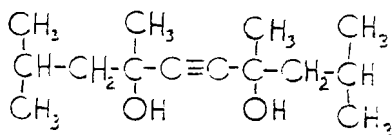
ALKYL AMMONIUM
DODECYL BENZENE SULFONATE



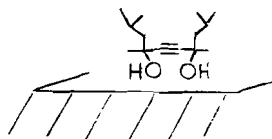
U.K. PAT. 1,072,702
(GERGY, 1967)

FIGURE 10

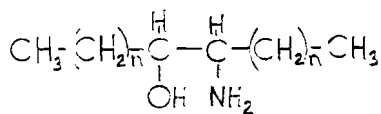
ALKYLDIOLS/ AMINO ALKANOLS



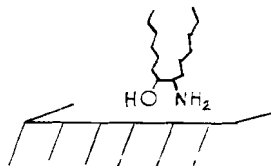
TETRAMETHYL - 5 - DECYN - 4,7 -
DIOL



U.S. PAT. APPLN. 264,760
(I.B.M., 1982)



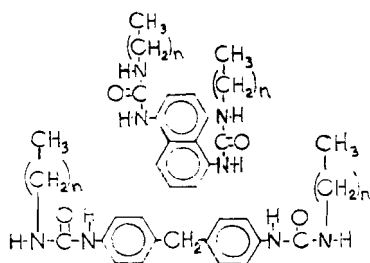
VICINAL AMINOALKANOL



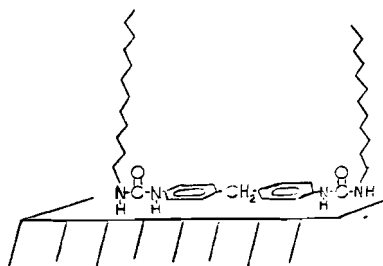
U.S. PAT. 4,167,420
(HENKEL, 1979)

FIGURE 11

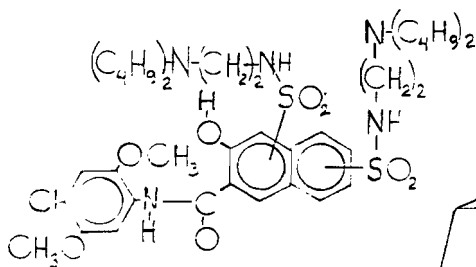
ALKYL DERIVATIVES OF COLORLESS POLYCYCLICS



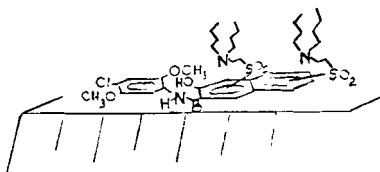
BIS (ALKYLUREA)
DERIVATIVE OF
DIPHENYL METHANE
(OR NAPHTHALENE)



U.S. PAT. 4,294,620
(BASF, 1981)

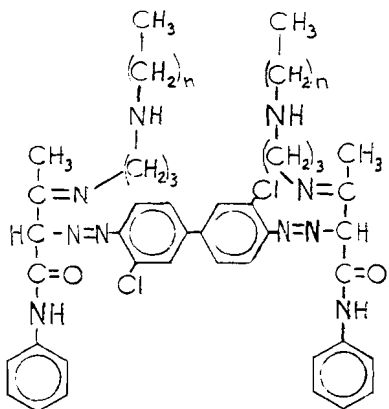


BIS (DIBUTYL AMINE)
DERIVATIVE OF
NAPHTHALENE

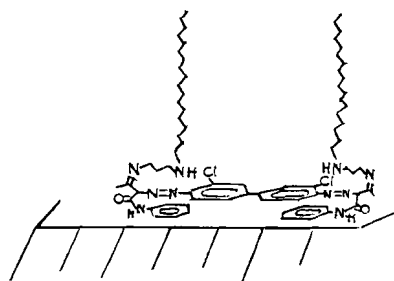


U.S. PAT. 4,317,682
(TOYO INK, 1982)

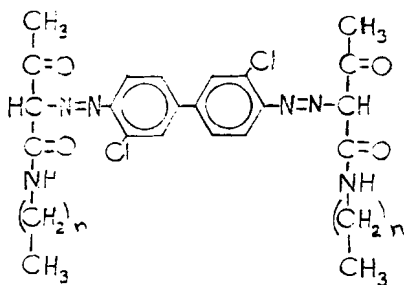
FIGURE 12
 ALKYL DERIVATIVE OF PIGMENTS (YELLOWS)



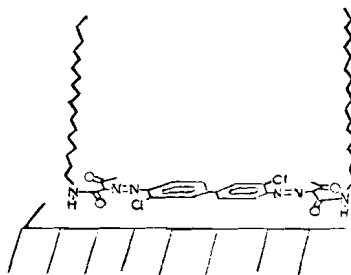
BIS (ALKYL KETIMINE)
 DERIVATIVE OF
 AAA YELLOW



U.S. PAT. 3,532,520
 (I.C.I., 1970)

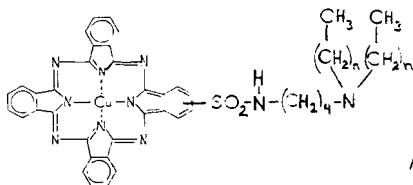


BIS (ALKYL AMIDE)
 DERIVATIVE OF YELLOW

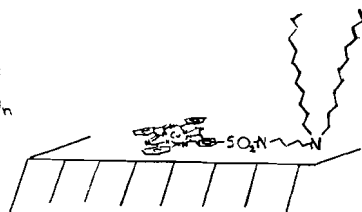


U.K. PAT. 1,139,294
 (I.C.I., 1969)

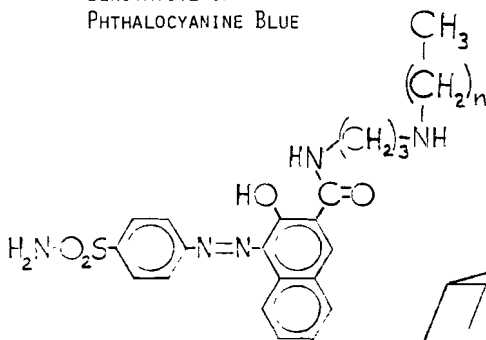
FIGURE 13
 ALKYL DERIVATIVES OF PIGMENTS (BLUE OR RED)



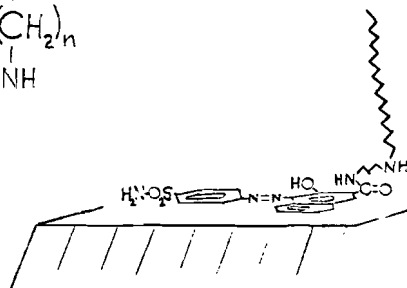
DIALKYL AMINE
 DERIVATIVE OF
 PHTHALOCYANINE BLUE



U.S. PAT. 4,313,766
 (CIBA-GEIGY, 1982)



ALKYL DERIVATIVE OF AN
 AZO RED



U.S. PAT. 3,446,641
 (I.C.I., 1969)