

MACROMOLECULAR DYES. OLIGOMERIC AND UNSATURATED DYES FOR U.V. CURING

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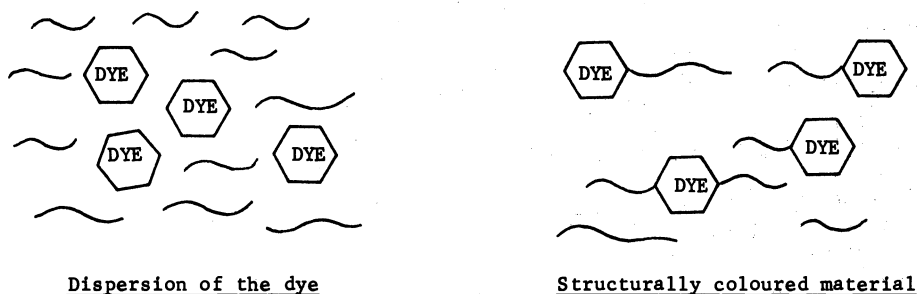
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Abstract : The synthesis and the properties of various macromolecular dyes are reported. They have been obtained by polymerization, polycondensation or chemical modification. Macromolecular dyes with double bonds in the chain are described ; they can be U.V. cured with a very low photoinitiator content.

Until now the processes used to colour materials have not implied a real chemical linkage between the macromolecules of the material and the molecules of the dye. The dye is either mixed with all the compound (colouration in the bulk) or deposited on the surface of the material (dyeing of fibers for instance).

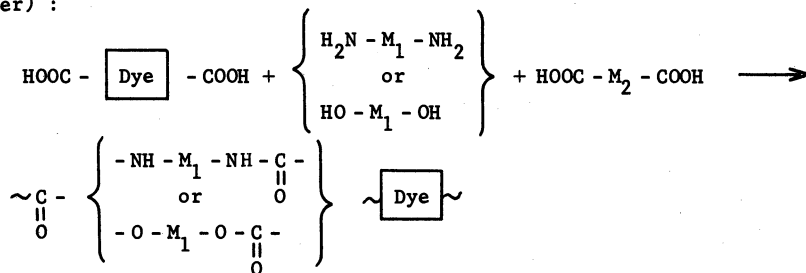
In our process the dye is a component of the macromolecular chain in which it has been introduced either by polycondensation or by polymerization. The difference between our process and classical ones is shown in figure 1.

Figure 1

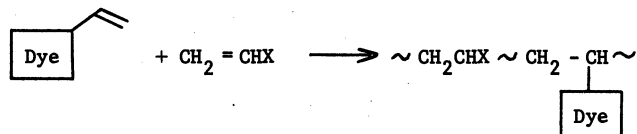


The processes of copolycondensation and copolymerization are shown below :

1 - Synthesis of a structurally coloured material by copolycondensation (polyamide or polyester) :



2 - Synthesis of a structurally coloured material by copolymerization :

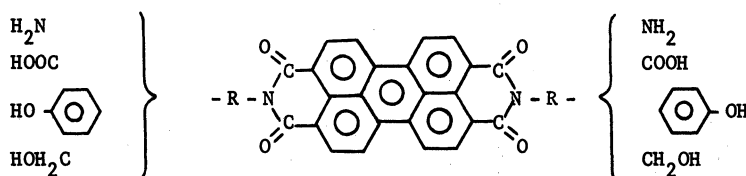
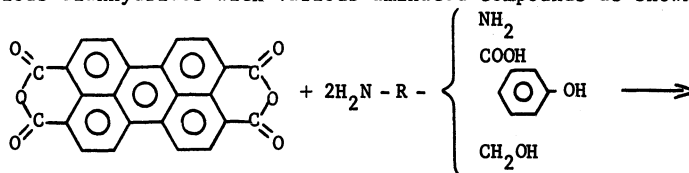


About 300 new copolymerizable or copolycondensable dyes have been synthesized. The whole range of colours has been covered and each of these dyes can be either copolycondensed or copolymerized with classical monomers. The following self coloured materials have been prepared

- polyamides (1, 2)
- aromatic polyesters (3, 4)
- polyurethanes (5)
- polyethers (6)
- various polyvinyl and polyacrylic materials (7, 8)

It is not possible to report the structures of all the dyes that have been used for each material. Only two examples will be developed : dyes for polyamides and dyes for polyvinyl compounds.

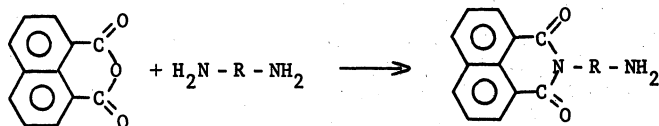
Dyes for polyamides and for some other self coloured polycondensates have been prepared by reacting various dianhydrides with various aminated compounds as shown below :



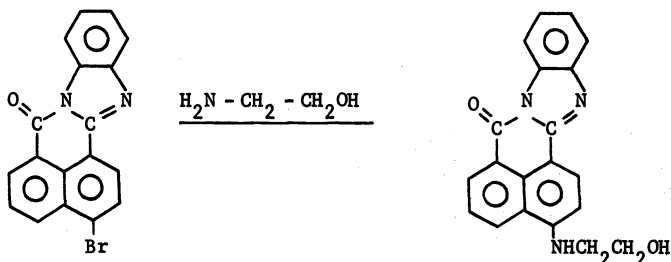
As it can be seen the method allows the synthesis of reactive dyes with very different end groups : these dyes can be used to prepare self coloured polyamides, polycarbonates and polyesters.

The synthesis of an unsaturated dye is reported below. This is a two stage process :

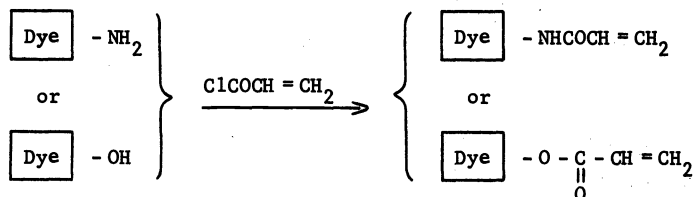
- First stage : Modification of a commercial dye in order to introduce in its structure an amino or a hydroxy group.



or



- Second stage : Reaction of the amino or of the hydroxy group with acryloyl chloride or anhydride :



After this very short description of some synthesis the main qualities required of a dye to be copolycondensed or copolymerized are reported below. The first set of qualities relate to a monomeric dye for polyamide, i.e. to a dye which will be copolycondensed in the melt or by interfacial technics.

1 - Thermal stability :

The dye must be stable up to 350°C as both copolycondensation and spinning are performed between 250 and 300°C.

2 - Geometry :

Linear dyes in order to avoid a perturbation of chain arrangements.

3 - Colour intensity : as large as possible.

4 - Solubility :

At least slightly soluble in the melt comonomers for the polycondensations in the bulk. Easily scattered for the interfacial polycondensations.

5 - Chemical properties :

No interference with the comonomers or the polycondensate.

High reactivity of the end groups.

This reactivity is tested by reacting the dye with a model compound.

We will not report any information relative to the copolycondensation or to the copolymerization for the simple reason that our method does not require any modification of the industrial processes.

After each copolymerization or copolycondensation it has been verified that the dye was really included in the chain and not only dispersed in the material. The tests used for this control are reported below.

a) The coloured material is solubilized in a liquid which is a solvent of the macromolecular compound but a non solvent of the dye. If the molecules of the dye are really included in the chains the whole solution is coloured ; if not the dye deposits at the bottom of the beaker.

b) The material is extracted by a liquid which is a solvent of the dye but a non solvent of the macromolecular compound. If the molecules of the dye are included in the chain the solution remains uncoloured ; if not the dye is extracted.

c) The same observations can be made when a solution of the material is submitted to a thin layer chromatography as shown in the slide.

d) Comparative copolycondensations have been performed with a dye having reactive end groups and a dye having exactly the same structure but with inactive end groups. In the first case tests a and b are positive and in the second case the tests are always negative.

e) The plot of the intrinsic viscosity against the dye content always exhibits a maximum when the dye is included in the chains ; on the other hand, when it is only dispersed the curve decreases continuously.

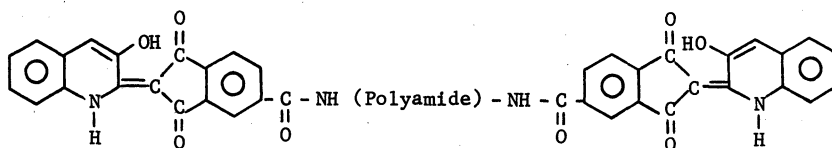
To conclude it can be said that :

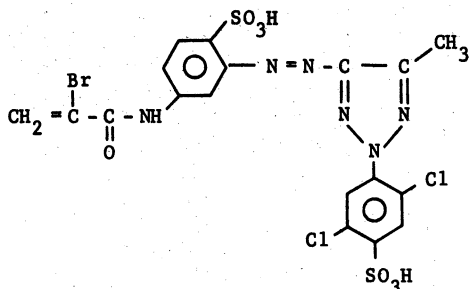
- Our method does not require any modification of the industrial reactors and processes and uses very classical dyes which have only to be slightly modified. The modification is generally easy.

- Thanks to this process, self coloured materials with completely new properties can be obtained.

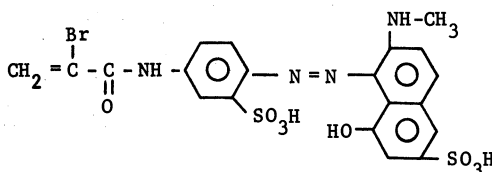
In order to improve the adaptability of this process to commercial requirements we have prepared and patented self coloured oligomers which are mixed with the material before spinning or molding. Some examples are reported below (3, 6).

a) Oligoamide : $1000 < \bar{M} < 1500$.

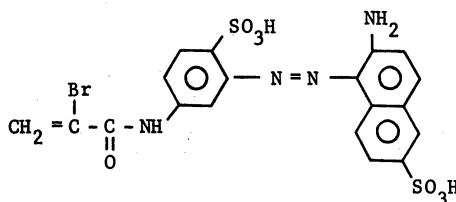




Yellow LANASOL 4G



Red LANASOL 5B



Orange LANASOL G

From the various copolymerizations the following general conclusions can be drawn :
 The molecular weights are kept in the range 4500-5000 by using a transfer agent.
 The yields are above 95 % and intrinsic viscosities are almost independent of the concentration of the dye and depend only on the transfer agent concentration.
 The conversion of the dye during the copolymerization is about 95 %.
 Copolymers with a dye content as high as 15 % have been obtained with a conversion of the dye over 95 %. However when the dye content is over 15 % the copolymer is aquosoluble.

We can say as follows concerning the photocuring :

Most of the dyes and photoinitiators absorb in the same wave length area ; however the absorption of the copolymers containing 10 % of dye is negligible compared with the absorption of photoinitiators.

All the compositions contain about 40 % of coloured unsaturated oligomers. Films with a thickness above 15 μ and a photoinitiator content of 1 % have been photocured in 0.1 to 1 second. Their mechanical properties and their adhesion to the metal are satisfactory. In our opinion, the fact that with our compositions only a very low photoinitiator content is required is due to the following reasons :

The absorption spectrum of each composition is very well known and allows a better choice of the photoinitiator. In the case of non soluble pigments the determination is much more difficult.

In classical processes due to their high content the pigments acts as a screen and part of the photoelectric energy is wasted but in our process the medium is very homogeneous and highly favorable to copolymerization. Moreover contrary to classical processes the coloured unsaturated oligomer takes part in the copolymerization.

This process has been patented (10).

However some severe criticisms can be made about the preceeding process :

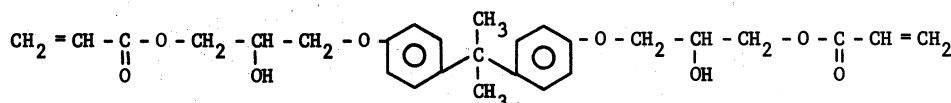
The dye content is too small for industrial uses (10 % in the coloured oligomer, 3 to 5 % in the film when the other components have been added).

The cost of the monomeric dyes is high.

This process requires the use of monofunctional acrylic monomers which are very unpleasant smelling and toxic compounds : 2 hydroxy ethyl acrylate which is commonly used gives rise to skin deceases. Moreover these compounds decrease the mechanical properties of the crosslinked film.

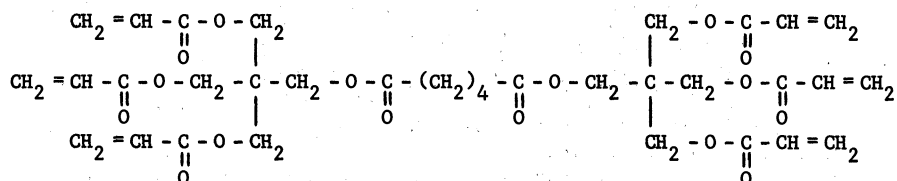
The french company PCUK has recently patented (11) a modification of this process which greatly improves its use and also the qualities of the resulting film. Its principle rests on the fact that the main low acrylic oligomers used incoating are the following :

Epoxy acrylate



obtained by reacting bis phenol A with epichlorhydrine and acrylic acid.

Polyester acrylate :



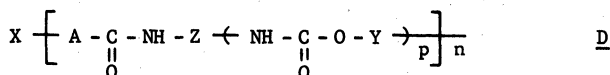
obtained by reacting adipic acid (or any fatty diacid) with pentaerythritol and acrylic acid.

Polyester/urethane/acrylate :

Obtained by reacting a long chain fatty acid with pentaerythritol, acrylic acid and a small amount of a diisocyanate.

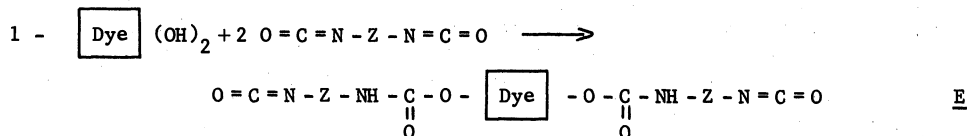
All these prepolymers have a molecular weight between 1000 and 3000 and a number of acrylic double bonds per mole between 2 and 6. Their viscosities are between some few poises and several hundred poises. Many other compounds are described. In the field of graphic arts the prepolymers "urethane" are particularly satisfactory because they provide flexibility and adhesivity to the film.

In the P.C.U.K. process the coloured, unsaturated oligomer has the following structure :

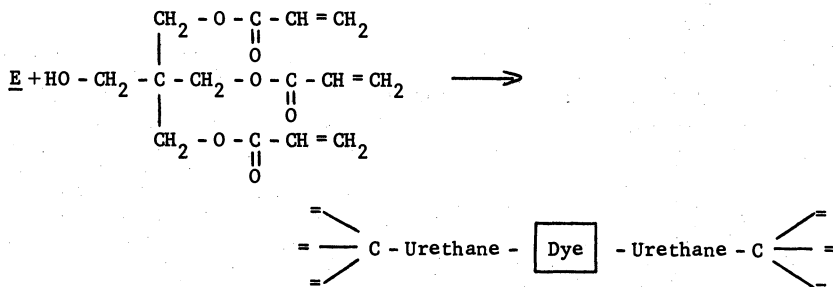


X is part of a dye ; -A- is -O- or NH ; Z is the aromatic or aliphatic part of a diisocyanate Z(-N=C=O)₂ such as hexamethylene diisocyanate or toluene diisocyanate ; Y is an unsaturated group.

D is obtained as follows :



2 - -N=C=O groups are reacted with pentacrythritol triacrylate :



Dyes belonging to the most varied classes have been used : azoic, anthraquinonic, perinonic, dyes derived from perylene tetracarboxylic, phthalocyanins, dioxazines, quinacridones, quinophtalones, thiazines, triphenylmethane derivatives, methinic dyes. These new unsaturated and coloured urethane-acrylate are satisfactory with regards to rheology, printability, intensity of colour, transparency and U.V. reactivity. However their stability to light is insufficient and must be improved.

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