

Production of pigment particles

The present invention relates to a process for producing pigment
5 particles, which comprises applying a polymerizable mixture containing a dye or an interference colorant either to a surface provided with indentations in the form of the desired pigment particles, polymerizing the mixture and then removing the polymerized pigment particles from the indentations, or to a smooth
10 surface in the form of the desired pigment particles, this form being predetermined in a known manner by means of a printing technique, polymerizing the mixture and then removing the polymerized pigment particles from the surface, with the exception of the production of pigment particles having a cholesteric liquid-
15 crystalline order structure by offset printing.

The present invention additionally relates to a device for producing pigment particles, to novel pigment particles obtainable by the abovementioned process, and to coating compositions comprising the novel pigment particles.
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Pigments are commonly prepared by precipitation reactions or by mechanical comminution of larger colored species. These pigment preparation methods produce pigment particles which differ in
25 form and size.

The prior German Patent Application 19532419.6 describes a process for preparing pigments having a cholesteric liquid-crystalline order structure by offset printing. In accordance with this
30 process it is possible to obtain pigment particles of regular form. The document makes no mention, however, of the preparation of pigments by other printing techniques nor of the preparation of pigments other than liquid-crystalline pigments.

35 For the preparation of high-grade pigmented coating materials, especially those whose perceived color is based on interference effects, it is advantageous to use pigment particles of defined, regular form and size.

40 It is an object of the present invention, therefore, to find a process for producing pigment particles of defined form.

We have found that this object is achieved by the process described at the outset.

The novel preparation process starts from a polymerizable mixture. This polymerizable mixture may, for example, comprise organic or inorganic dyes. These dyes are either themselves polymerizable, for example through polymerizable side chains on the chromophores, or the dyes are mixed with a polymerizable binder, so that they can be incorporated into a polymeric network. The choice of dye here depends on the subsequent use of the pigment. In principle, all dyes can be employed in the novel process. Advantageously, the dyes employed are either insoluble or can be incorporated covalently into the polymeric network.

Suitable dyes are described in more detail below.

Particularly suitable azo dyes are mono- or disazo dyes, for example those with a diazo component derived from an aniline or from a five-membered aromatic heterocyclic amine whose heterocyclic ring includes one to three heteroatoms selected from the group consisting of nitrogen, oxygen and sulfur, which compound may be fused with a benzene, thiophene, pyridine or pyrimidine ring.

Examples of important mono- and disazo dyes are those whose diazo component is derived, for example, from an aniline or from a heterocyclic amine from the pyrrole, furan, thiophene, pyrazole, imidazole, oxazole, isoxazole, thiazole, isothiazole, triazole, oxadiazole, thiadiazole, benzofuran, benzothiophene, benzimidazole, benzoxazole, benzothiazole, benzisothiazole, pyridothiophene, pyrimidothiophene, thienothiophene or thienothiazole series.

Diazo components deserving particular mention are those originating from an aniline or from a heterocyclic amine from the pyrrole, thiophene, pyrazole, thiazole, isothiazole, triazole, thiadiazole, benzothiophene, benzothiazole, benzoisothiazole, pyridothiophene, pyrimidothiophene, thienothiophene or thienothiazole series.

Also of importance are azo dyes with a coupling component from the aniline, aminonaphthalene, aminothiazole, diaminopyridine or hydroxypyridone series.

The monoazo dyes are known per se and have been described in large numbers, for example in K. Venkataraman "The Chemistry of Synthetic Dyes", Vol. VI, Academic Press, New York, London, 1972, or in EP-A-201 896.

Other dyes which can be used with advantage are anthraquinone, coumarin, methine, azamethine and quinophthalone dyes.

Suitable anthraquinone dyes are described, for example, in
5 D.R. Waring, G. Hallas "The Chemistry and Application of Dyes",
pages 107 to 118, Plenum Press, New York, London, 1990.

Suitable coumarin dyes are described, for example, in Ullmanns
Encyklopädie der technischen Chemie, 4th edition, Volume 17,
10 page 469.

Suitable methine or azamethine dyes are described, for example,
in US-A-5 079 365 and WO-A-9219684.

15 Suitable quinophthalone dyes are described, for example, in
EP-83 553.

The term polymerization is to be understood as referring to any
kind of polymer synthesis reaction, thus including chain addition
20 polymerizations, step-growth addition polymerizations and conden-
sation polymerizations.

In addition to the dyes or interference colorants, the polymeri-
zable mixture can include various additives which are customary
25 in the art of surface coatings or printing inks, such as poly-
merizable binders, reactive diluents, dispersion auxiliaries,
polymeric binders, fillers, diluents and polymerization initia-
tors.

30 Particularly suitable additives are polymeric binders and/or
monomeric compounds which can be converted by polymerization into
a polymeric binder. Examples of suitable such materials are sili-
cones (which may be polyether- or polyester-modified), polyure-
thanes, cellulose esters and polyesters which are soluble in or-
35 ganic solvents. Particular preference is given to the use of cel-
lulose esters, such as cellulose acetobutyrate.

Particularly suitable polymeric binders are those which contain
reactive crosslinkable groups such as acrylic, methacrylic,
40 α -chloroacrylic, vinyl, vinyl ether, epoxide, cyanate, isocyanate
or isothiocyanate groups. Monomeric materials are also suitable
as binders, especially the reactive diluents known from paint
preparations such as, for example, hexanediol diacrylate or bisp-
henol A diacrylate. Even small amounts of such substances -
45 usually just from 0.1 to 1% by weight - bring about a consider-
able improvement in flow viscosity. At the same time, these mate-

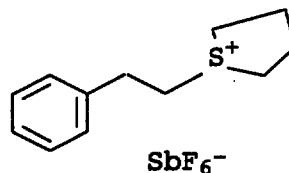
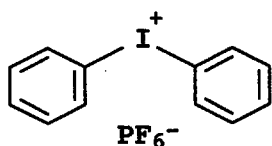
rials have a great influence on the mechanical properties of the hardened pigment particles.

- Examples of suitable solvents or diluents are esters, especially
5 acetic esters, alcohols, lactones, aliphatic and aromatic hydrocarbons, amides, N-alkylpyrrolidones, especially N-methylpyrrolidone, tetrahydrofuran and dioxane. Water as well can in some cases be employed with advantage as diluent.
- 10 Furthermore, the polymerizable mixtures may contain polymerization initiators, which decompose either thermally or photochemically and thus bring about the curing of the coating. Among thermal polymerization initiators, preference is given to those
15 decomposing at between 20 and 180°C, particularly preferably between 50 and 80°C, to initiate the polymerization. For photochemical curing, all photoinitiators can be used in principle. In particular, mixtures of different initiators are also employed in order to improve through-curing. Examples of highly suitable photoinitiators are benzophenone and its derivatives, such as alkyl-
20 benzophenones, halomethylated benzophenones or 4,4'-bis(dimethylamino)benzophenone, and also benzoin and benzoin ethers such as ethyl benzoin ether, benzil ketals, such as benzil dimethyl ketal, acetophenone derivatives, such as hydroxy-2-methyl-1-phenylpropan-1-one, and hydroxycyclohexyl phenyl ketone. Acylphosphine
25 oxides, such as 2,4,6-trimethylbenzoyldiphenylphosphine oxide, are very particularly suitable. Among photochemically activatable polymerization initiators, preference is given to using those which exhibit no yellowing effect.
- 30 Other particularly preferred polymerization initiators are boron alkyl compounds, and also peroxides such as dibenzoyl peroxide and di-tert-butyl peroxide.

The photoinitiators, which depending on the intended use of the
35 novel pigments are advantageously employed in amounts from 0.01 to 15% by weight, based on the polymerizable components, can be used as individual substances or, on account of advantageous synergy effects, in combination with one another.

- 40 For cationic polymerizations, it is preferred to employ initiators having charged structures. Use is made in particular of substances which are in some cases employed in combination with acylphosphine oxides, for example:

5



and derivatives of these compounds.

- 10 If desired, UV stabilizers and weathering stabilizers can also be added to the polymerizable mixtures. Examples of suitable such compounds are derivatives of 2,4-dihydroxybenzophenone, of 2-cyano-3,3-diphenyl acrylate, of 2,2',4,4'-tetrahydroxybenzophenone and of orthohydroxyphenylbenzotriazole, salicylic esters, 15 orthohydroxyphenyl-S-triazines [sic] or sterically hindered amines. These substances can be employed individually or, preferably, in the form of mixtures.

Examples of suitable fillers are rutile, anatase, chalk, talc and 20 barium sulfate.

Dispersion auxiliaries have a positive influence on the flow viscosity of the polymerizable mixture and on the miscibility of the individual components of this mixture. All customary commercial 25 dispersion auxiliaries can be employed.

Particularly suitable dispersion auxiliaries are those based on a succinimide, succinate or succinic anhydride structure, as are described in the prior German Patent Application 19532419.6.

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The polymerizable mixture can include dyes and/or interference colorants. Since the form of such interference pigments is particularly critical, the novel process is particularly suitable for preparing such pigments.

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Particularly advantageous interference colorants are cholesteric liquid-crystalline compositions.

Cholesteric liquid-crystalline phases can be produced either 40 using chiral liquid-crystalline compounds or by adding suitable chiral dopants to achiral liquid-crystalline compounds.

The cholesteric liquid-crystalline compositions employed in the novel preparation process preferably comprise the following components: 45

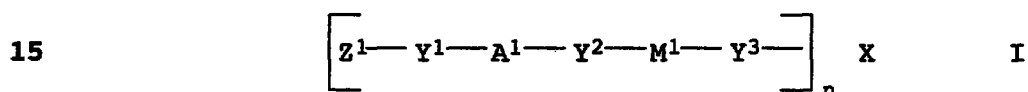
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- a) at least one chiral liquid-crystalline polymerizable monomer,
or
- b) at least one achiral liquid-crystalline polymerizable monomer
5 and a chiral compound.

In this context, particularly suitable such components in each case are those whose reactive groups mean that they can be converted or incorporated into a polymeric network.

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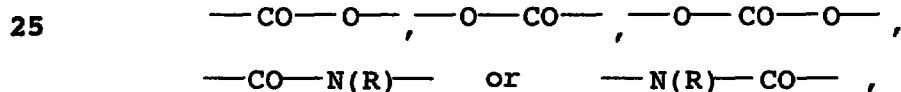
Particularly suitable chiral liquid-crystalline polymerizable monomers a) are those of the general formula I



where

- 20 Z^1 is a polymerizable group or a radical which carries a polymerizable group,

Y^1, Y^2 and Y^3 are chemical bonds, oxygen, sulfur,



- A^1 is a spacer,

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M^1 is a mesogenic group,

X is an n-valent chiral radical,

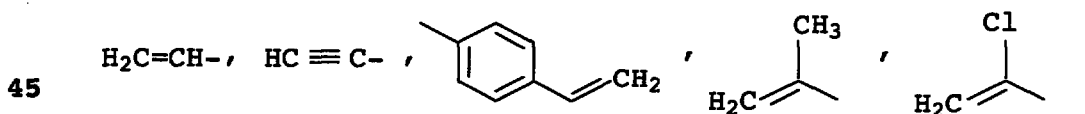
- 35 R is hydrogen or C_1 - C_4 -alkyl,

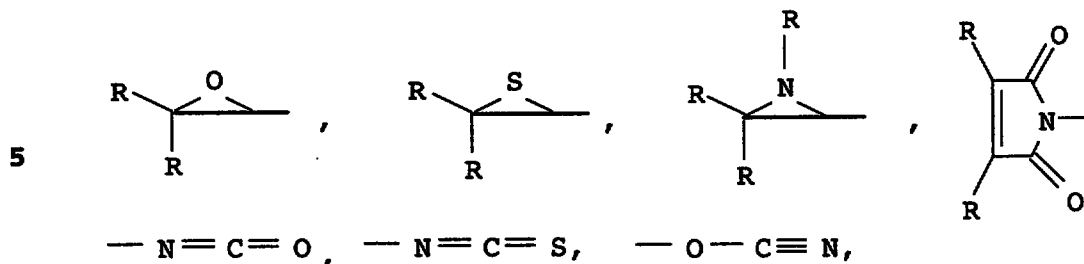
n is 1 to 6,

and Z^1, Y^1, Y^2, Y^3, A^1 and M^1 can be identical or different.

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Preferred radicals Z^1 are:





where R can be identical or different and is hydrogen or C¹-C⁴-alkyl [sic] such as methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl or tert-butyl. Among the reactive polymeriza-

15 ble groups, the cyanates are able to trimerize spontaneously to form cyanu-rates, and are therefore preferable. Polymerization of the other groups mentioned requires additional compounds having complementary reactive groups. For example, isocyanates can polymerize with alcohols to form urethanes and with amines to form

20 urea derivatives. Similar comments apply to thiiranes and aziridines. Carboxyl groups can be condensed to form polyesters and polyamides. The maleimido group is particularly suitable for free-radical copolymerization with olefinic compounds such as styrene. These complementary reactive groups can be either pre-

25 sent in a second novel compound, which is mixed with the first, or incorporated into the polymeric network by means of auxiliary compounds containing two or more of these complementary groups.

Y¹-Y³ are as defined at the outset, the term chemical bond refer-

30 ring to a single covalent bond.

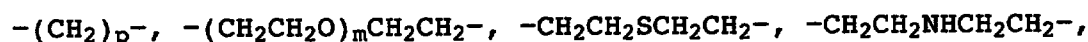
Particularly preferred groups Z¹-Y¹ are acrylate and methacrylate.

Suitable spacers A¹ are all groups known for this purpose, and ge-

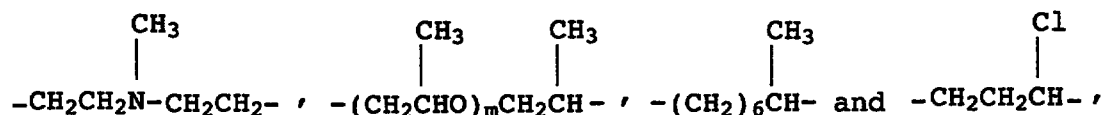
35 nerally contain 2-30, preferably 2-12, carbon atoms and consist of linear aliphatic groups. Their chain can be substituted by, for example, (nonadjacent) O, S, NH or NCH₃. Suitable substituents for the spacer chain are fluorine, chlorine, bromine, cyano, methyl and ethyl.

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Examples of representative spacers are:



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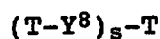


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where

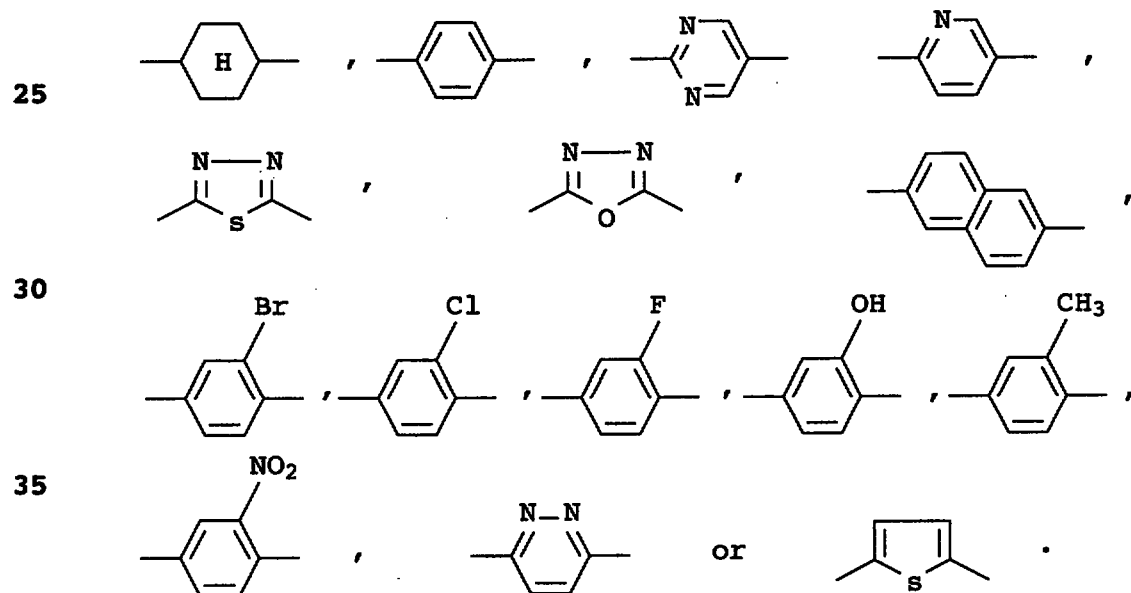
m is 1-3 and

p is 1-12.

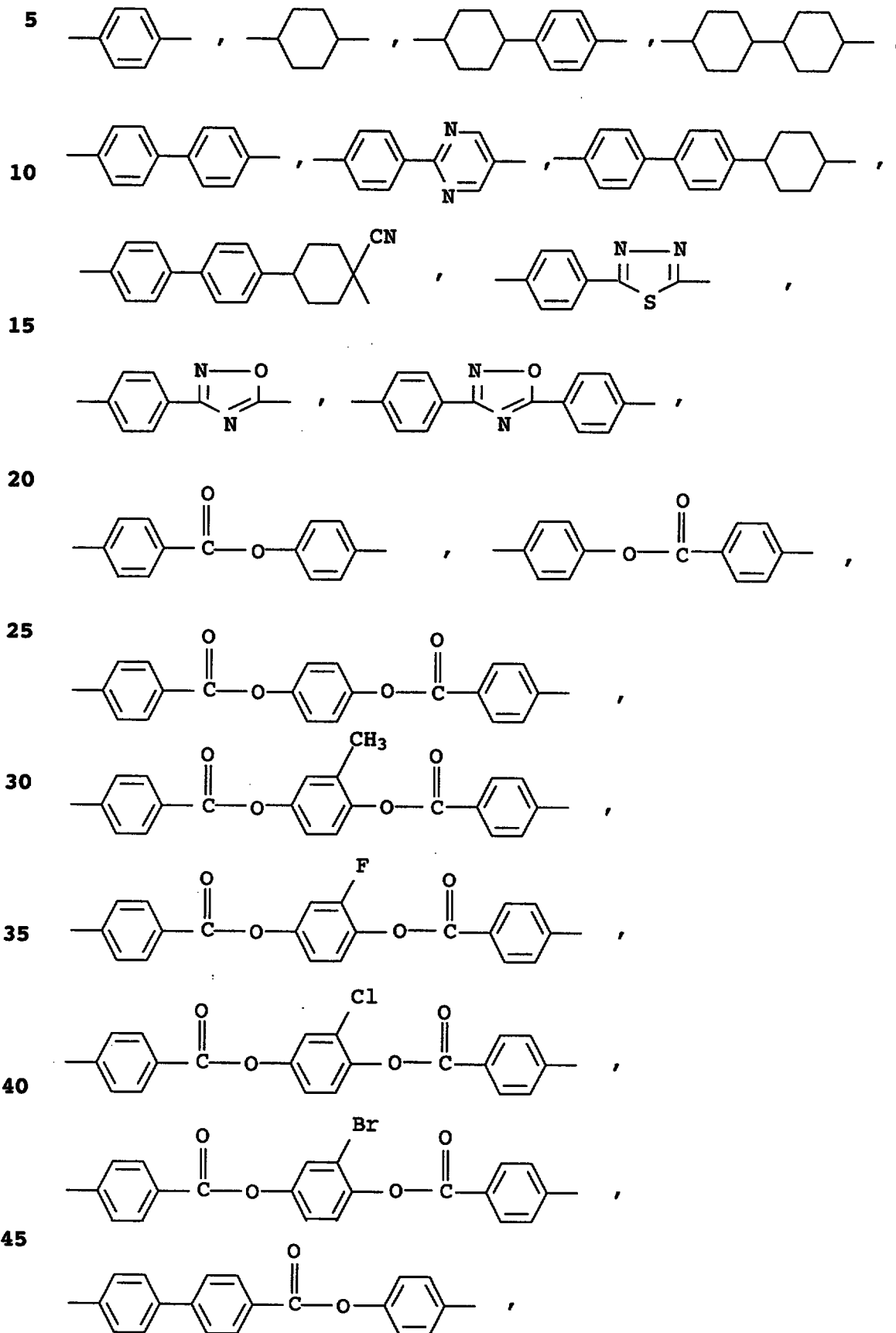
10 The mesogenic group M^1 preferably has the structure

15 where Y^8 is a bridging link as for Y^1 , s is 1-3 and T may be identical or different at each occurrence and is a divalent isocycloaliphatic, heterocycloaliphatic, isoaromatic or heteroaromatic radical.

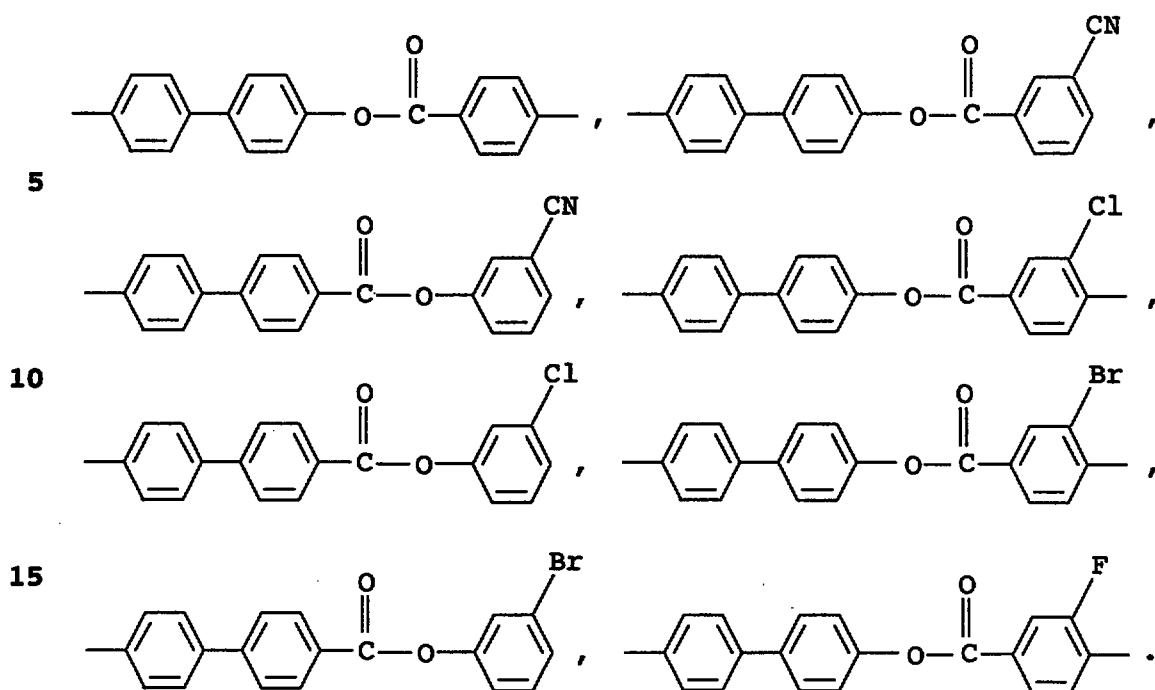
20 T can also be a ring system substituted by fluorine, chlorine, bromine, cyano, hydroxyl or nitro, preferably:



Particularly preferred mesogenic groups M^1 are as follows:



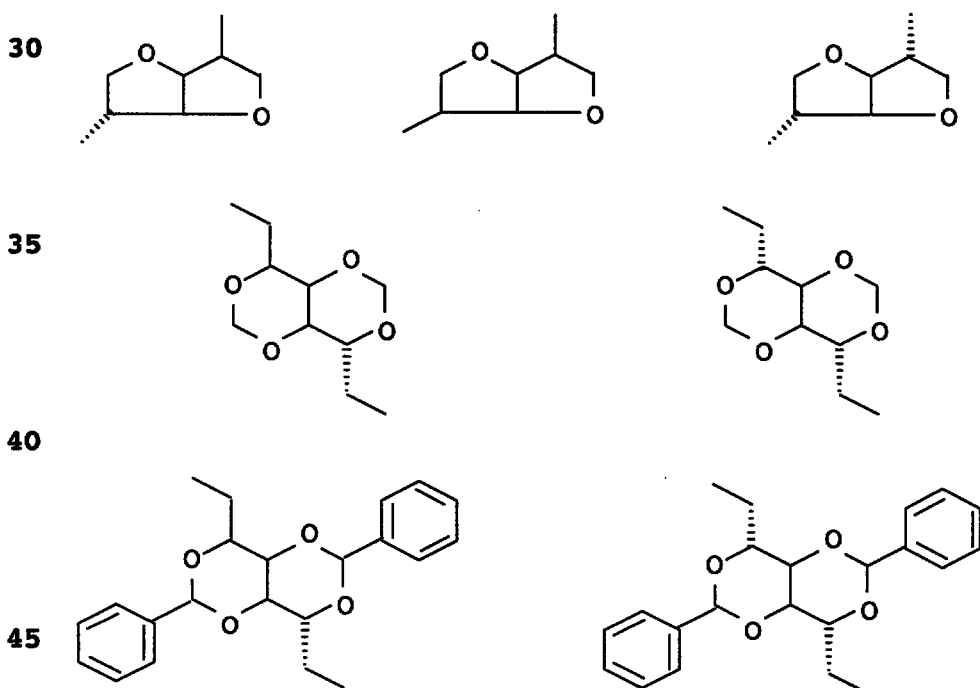
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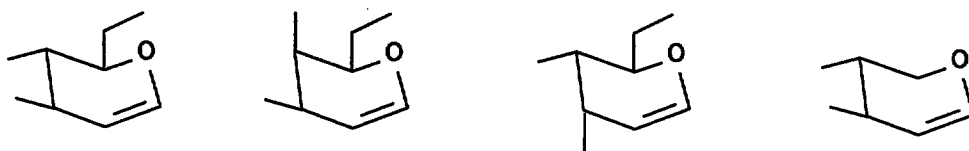
For reasons inter alia of availability, particularly preferred
 20 chiral radicals X of the compounds of the general formula I are
 those derived from sugars, binaphthyl or biphenyl derivatives,
 and optically active glycols, dialcohols or amino acids. Sugars
 deserving particular mention are pentoses, hexoses and derivati-
 ves thereof.

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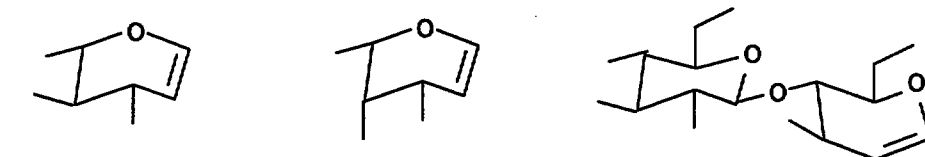
Examples of radicals X are the following structures, the terminal
 lines in each case denoting the free valencies.



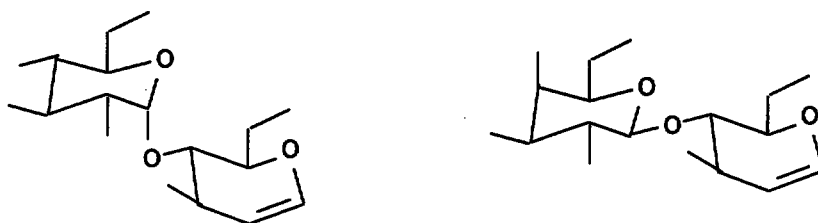
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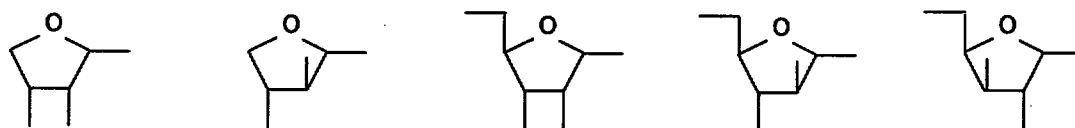
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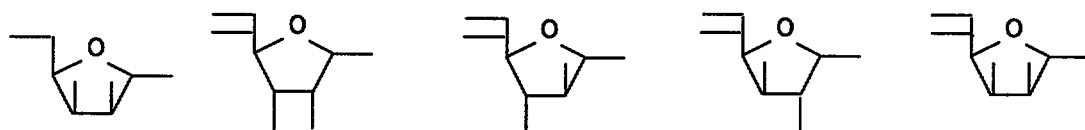
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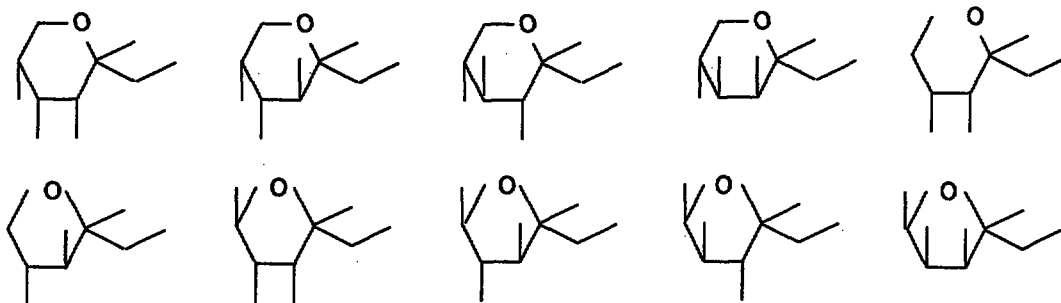


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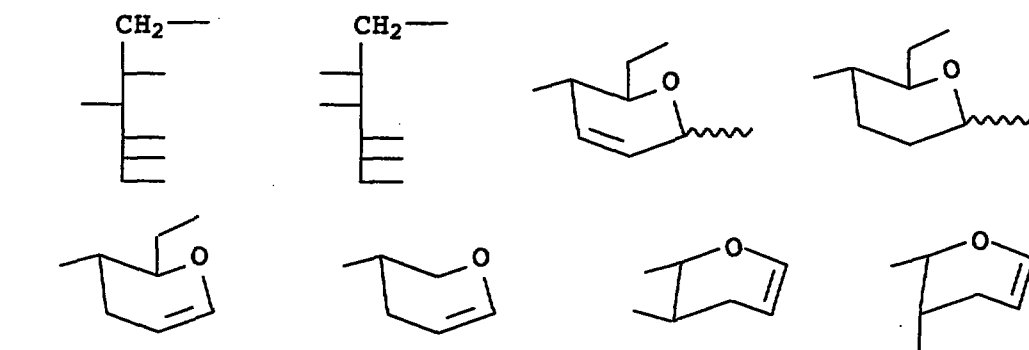
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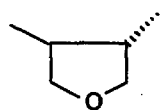


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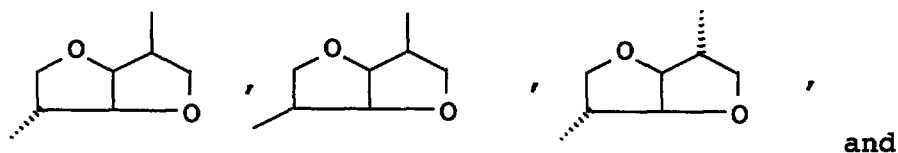


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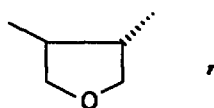


Particular preference is given to

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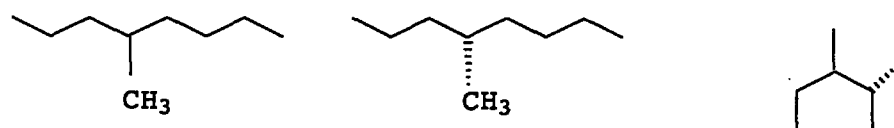
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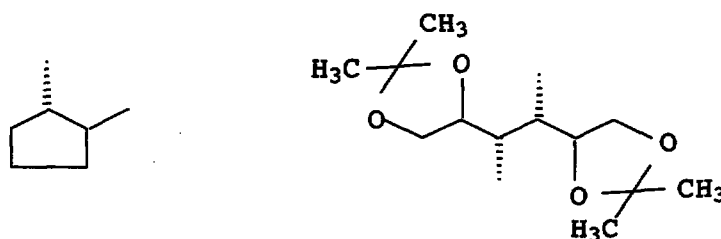
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Also suitable are chiral groups containing the following structures:

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Further examples are given in EP-A 0 739 403.

R can be hydrogen and also methyl, ethyl, n-propyl, isopropyl,
5 n-butyl, isobutyl, sec-butyl and tert-butyl;

n is preferably 2.

Among the achiral liquid-crystalline polymerizable monomers b),
10 particularly suitable examples for the cholesteric liquid-crystalline composition are those of the general formula II



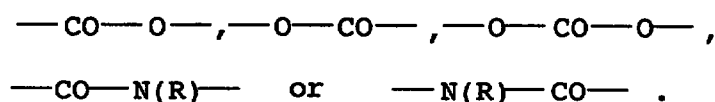
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where

Z^2 and Z^3 are polymerizable groups or contain a polymerizable
20 group, and

Y^4, Y^5, Y^6 and Y^7 are chemical bonds, oxygen, sulfur,

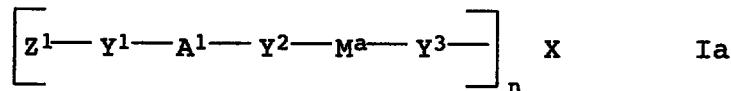
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The polymerizable groups, bridging links Y^4-Y^7 , spacers and meso-
genic groups are subject to the same preferences as for the cor-
30 responding variables in the general formula I.

In addition to an achiral liquid-crystalline monomer, the chole-
steric liquid-crystalline composition b) contains a chiral com-
pound, preferably of the formula Ia

35



where $Z^1, Y^1, Y^2, Y^3, A^1, X$ and n are as defined above and M^a is a
40 divalent radical containing at least one heterocyclic or isocy-
clic ring system.

In this context, the molecule section M^a resembles the mesogenic
groups described, since in this way particularly good compati-
45 bility with the liquid-crystalline compound is achieved. However, M^a
need not actually be mesogenic, since the compound Ia is intended
to bring about an appropriate twisting of the liquid-crystalline

phase merely by means of its chiral structure. Preferred ring systems in M^a are the abovementioned structures T.

The polymerizable mixture can be processed to give pigment particles of defined structure in two ways. Either the mixture is applied to a surface provided with indentations and is then polymerized, or the forming operation takes place by a printing technique, in which the mixture is printed onto a smooth surface and then polymerized.

10

For the latter case, a variety of printing techniques are suitable which enable application of ink in the size and form which is desired for the pigment. Suitable examples are offset, screen, relief, gravure and flexographic printing. The important factor is that suitable auxiliaries are used to adjust the viscosity to a level where the mixture can be printed without running. In the case of cholesteric liquid-crystalline pigments, additional care should be taken that the auxiliaries do not adversely affect the liquid-crystalline structure and that spontaneous orientation of the liquid crystals on the surface is possible. Suitable auxiliaries are specified in the prior German Patent Application 19532419.6.

The term smooth surface implies a surface which has no indentations in the order of size of the pigment particles which are to be produced, and which is not absorbent. Examples of suitable surfaces are those of plastic films or metal sheets.

For the production of pigment particles by application of a polymerizable mixture to a surface provided with indentations, a particularly suitable surface is that of films, especially plastic films, since these can easily be structured in the desired manner. Suitable methods of structuring, ie. the production of the indentations, are the methods known for the production of printing plates, for example.

The indentations may be on a planar surface but can also, preferably, be on the surface of a rotatable roller. In this way the pigment particles can be produced in a continuous process. A preferred process for producing pigment particles comprises introducing the polymerizable mixture continuously into indentations on the surface of a rotating roller or of a roller belt, polymerizing it by exposure to light and then removing it from the surface of the roller or roller belt by means of a suction or brushing device. In this context, the dimension of the roller and its rotational speed should be chosen such that the liquid polymerizable mixture applied has through-cured sufficiently before it

reaches the concluding suction or brushing station. Other factors affecting this, of course, are the intensity of exposure, the length of the exposure section and the temperature, for example. In order to obtain good throughput and a rapid polymerization

5 rate, it is often advantageous to carry out polymerization at relatively high temperatures, for example at 30-150°C, especially 50-100°C. However, the process can also be carried out at other temperatures, with the ambient temperature normally being sufficient.

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The exposure light source depends on the nature of the polymerizable groups and the photoinitiator possibly used. Suitable exposure light sources are all those which can be used in plastics technology.

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The polymerizable mixture can be polymerized not only by exposure to light but also by electron beams, or, given appropriate polymerizable groups, can be induced thermally.

20 The pigment particles produced by the novel process can have various forms and sizes. A plateletlike structure is particularly advantageous for pigments whose perceived color is based on interference effects. In the case of these pigments, the perceived color depends on the viewing angle. The plateletlike structure
25 re enables a uniform arrangement of the pigment particles in the colored layer, giving rise to the same kind of reflection from numerous pigment particles and thus to a homogeneous perceived color.

30 A particular advantage of the novel process is the possibility of producing pigment platelets of identical form and size. The identical form of the novel pigments, especially the interference pigments, gives the perceived color a particular brilliance.

35 The novel pigments are suitable for use as color-imparting constituents of coating compositions such as printing inks, emulsion paints and lacquers. Such coating compositions may include further customary additives. Examples of suitable additives are given in the prior German Patent Application 19532419.6, to which
40 express reference is made. Paints containing the novel pigments are particularly suitable for painting commodity articles, especially vehicles such as cars, motorbikes, etc.

A preferred device for producing pigment particles comprises

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- a rotating roller or a roller belt with a surface containing indentations in the form of the desired pigment particles,
- 5 - a device for applying a polymerizable mixture containing a dye or an interference colorant to the roller or the roller belt,
- a device for exposing the polymerizable mixture to light, and
- 10 - a device for removing the polymerized pigment particles from the indentations in the roller or roller belt and for collecting the pigment particles.

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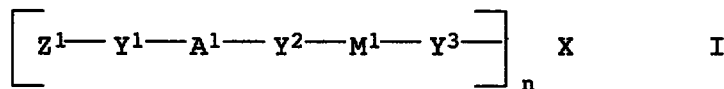
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We claim:-

1. A process for producing pigment particles, which comprises
 5 applying a polymerizable mixture containing a dye or an interference colorant either to a surface provided with indentations in the form of the desired pigment particles, polymerizing the mixture and then removing the polymerized pigment particles from the indentations, or to a smooth surface in the form of the desired pigment particles, this form
 10 being predetermined in a known manner by means of a printing technique, polymerizing the mixture and then removing the polymerized pigment particles from the surface, with the exception of the production of pigment particles having a cholesteric liquid-crystalline order structure by offset printing.
 15
2. A process as claimed in claim 1, wherein the polymerizable mixture comprises a cholesteric liquid-crystalline composition as interference colorant.
 20
3. A process as claimed in claim 2, wherein the cholesteric liquid-crystalline composition comprises the following components:
 25
 - a) at least one chiral liquid-crystalline polymerizable monomer, or
 - b) at least one achiral liquid-crystalline polymerizable monomer and a chiral compound.
 30
4. A process as claimed in claim 3, wherein the chiral liquid-crystalline polymerizable monomers a) have the structure of the general formula I
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where:

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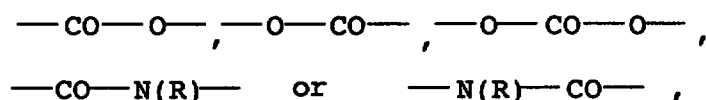


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Z^1 is a polymerizable group or a radical which carries a polymerizable group,

Y^1, Y^2 and Y^3 are chemical bonds, oxygen, sulfur,

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A^1 is a spacer,

M^1 is a mesogenic group,

X is an n-valent chiral radical,

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R is hydrogen or C_1 - C_4 -alkyl,

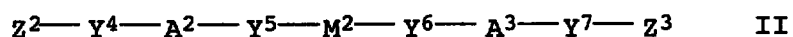
n is 1 to 6,

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and Z^1, Y^1, Y^2, Y^3, A^1 and M^1 can be identical or different.

5. A process as claimed in claim 3, wherein the achiral liquid-crystalline polymerizable monomers b) have the structure of the general formula II

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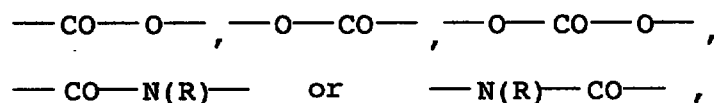
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where

Z^2 and Z^3 are polymerizable groups or contain a polymerizable group,

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Y^4, Y^5, Y^6 and Y^7 are chemical bonds, oxygen, sulfur,



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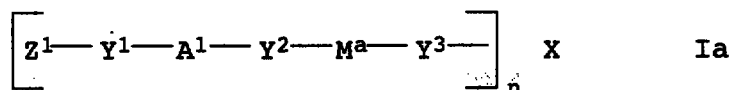
A^2 and A^3 are spacers, and

M^2 is a mesogenic group.

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6. A process as claimed in claim 3, wherein the chiral compounds b) are of the general formula Ia





- 5 where Z^1 , Y^1 , Y^2 , Y^3 , A^1 , X and n are as defined above and M^a is a divalent radical containing at least one heterocyclic or isocyclic ring system.
7. A process as claimed in any of claims 1 to 6, wherein the
10 surface provided with indentations is a film.
8. A process as claimed in any of claims 1 to 6, wherein the indentations are on the surface of a rotatable roller.
- 15 9. A process as claimed in any of claims 1 to 8, wherein the polymerizable mixture is polymerized by means of light.
10. A process as claimed in any of claims 1 to 9, wherein the polymerizable mixture is introduced continuously into indentations on the surface of a rotating roller or of a roller
20 belt, polymerized by exposure to light and then removed from the surface of the roller or the roller belt by means of a suction or brushing device.
- 25 11. A process as claimed in any of claims 1 to 10, wherein the pigment particles have a plateletlike structure.
12. Pigment particles obtainable by a process as claimed in any of claims 1 to 11.
- 30 13. A coating composition comprising pigment particles as claimed in claim 12.
14. A device for producing pigment particles, comprising
35 - a rotating roller or a roller belt with a surface containing indentations in the form of the desired pigment particles,
- a device for applying a polymerizable mixture containing a
40 dye or an interference colorant to the roller or the roller belt,
- a device for exposing the polymerizable mixture to light, and
- 45 - a device for removing the polymerized pigment particles from the indentations in the roller or roller belt and for collecting the pigment particles.

