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(54) **METHODE POUR PREPARER DES LAQUES OU DES VERNIS  
PIGMENTES POUR LA COLORATION DES VERRES DE  
CONTACT; LAQUES PIGMENTEES OU INCOLORES AINSI  
OBTENUS VERRES DE CONTACT COLORES A L'AIDE**

(54) **METHOD TO PREPARE PIGMENTED LACQUERS OR  
VARNISHES FOR THE COLORING OF CONTACT LENSES,  
THE PIGMENTED OR COLORLESS LACQUERS THUS  
OBTAINED AND THE CONTACT LENSES COLORED WITH  
SAID LACQUERS**

(57) Pigmented lacquers or varnishes for coloring contact lenses are prepared by prepolymerizing under UV radiation half of a mixture of: 60 to 70 weight % of N-vinyl-2-pyrrolidone, 8 to 12 weight % of hydroxyethyl methacrylate, 0.3 to 1 weight % of reticulant components, up to 13 weight % of cyclohexyl methacrylate or acrylate, 8 to 15 weight % of glycidyl acrylate or methacrylate, as binding agent, up to 1 weight % of acrylic or methacrylic acid, 0.1 to 0.5 weight % of UV photoinitiator of polymerization, under stirring and at ambient temperature, during a period of time sufficient to form a mass of oily consistency, which when radiation is turned off and is rapidly cooled in a -30°/-40° C bath, changes into a gel storable at low temperatures; extracting the free monomers from the gel until an easily malleable paste is formed; letting the paste settle at ambient temperature, so that it may lose by exudation the remainder of free monomers it might contain; dissolving this paste with part of the aforesaid mixture of liquid monomers without prepolymerization, in ponderal relation sufficient to form a solution at a temperature not higher than ambient temperature, then filtering and recovering a transparent, colorless and curable lacquer, to be kept between -18°/-25° C; and pigmenting the lacquer and mixing it with the necessary quantity of the chosen micronized pigments. The method of the invention enables to obtain pigmented or colorless lacquers or varnishes which are storable during periods of up to 6 months with no unfavorable changes and, consequently, ready to be used.



## ABSTRACT

Pigmented lacquers or varnishes for coloring contact lenses are prepared by prepolymerizing under UV radiation half of a mixture of: 60 to 70 weight % of N-vinyl-2-pyrrolidone, 8 to 12 weight % of hydroxyethyl methacrylate, 0.3 to 1 weight % of reticulant components, up to 13 weight % of cyclohexyl methacrylate or acrylate, 8 to 15 weight % of glycidyl acrylate or methacrylate, as binding agent, up to 1 weight % of acrylic or methacrylic acid, 0.1 to 0.5 weight % of UV photoinitiator of polymerization, under stirring and at ambient temperature, during a period of time sufficient to form a mass of oily consistency, which when radiation is turned off and is rapidly cooled in a  $-30^{\circ}/-40^{\circ}$  C bath, changes into a gel storable at low temperatures; extracting the free monomers from the gel until an easily malleable paste is formed; letting the paste settle at ambient temperature, so that it may lose by exudation the remainder of free monomers it might contain; dissolving this paste with part of the aforesaid mixture of liquid monomers without prepolymerization, in ponderal relation sufficient to form a solution at a temperature not higher than ambient temperature, then filtering and recovering a transparent, colorless and curable lacquer, to be kept between  $-18^{\circ}/-25^{\circ}$  C; and pigmenting the lacquer and mixing it with the necessary quantity of the chosen micronized pigments. The method of the invention enables to obtain pigmented or colorless lacquers or varnishes which are storable during periods of up to 6 months with no unfavorable changes and, consequently, ready to be used.

METHOD FOR COLORING CONTACT LENSES AND LENSES MADE BY  
THE SAME

The present invention refers to a method for preparing lacquers or varnishes for coating contact lenses, and to the contact lenses coated with such lacquers or varnishes.

This invention is very especially related to the preparation of inks or lacquers for contact lenses formed by polymeric substrates, which make up the lens itself and a layer of color or colored varnish, which is in turn integrated to a partially prepolymerized matrix formulated with monomers, the polymerization of which is completed "in situ". In this manner, the color layer and the substratus remain firmly consolidated or bound through covalent linkage. The fundamental advantages of this invention are the color durability, the lacquer versatility (it may be applied to flexible, hydrophilic and gas permeable lenses) regardless of their constituent chemical groups) and the simplicity of the preparation and application methods.

It is a well-known fact that colored contact lenses, also called "cosmetic" lenses, are mainly designed to enhance or modify the color of the eyes, by applying a layer of color that covers the iris.

The preliminary art includes several endeavors developed with the purpose of producing cosmetic contact lenses, including also ophthalmic prosthesis, of everlasting color. U.S. Patent No. 3,679,504 for instance, proposes the manufacture of soft contact lenses, of many layers or "sandwich" struc-

ture, being the color layer formed or deposited between two transparent layers of hydrophilic polymers (for instance, copolymers of ethyleneglycol monomethacrylate with less than 2% of ethyleneglycol dimethacrylate, (eventually in mixture with the diester) bound by means of an adhesive layer consisting in a mixture of polymerized monomers (of a composition equal or similar to that of said layers) deposited or interposed between the mentioned hydrogel layers. In term, the color layer is formed before the material or adhesive precursor mixture of monomers is deposited, starting from dyes or pigments applied, for instance, over one of the hydrogel formed layers. In this manner, the color layer is not in direct contact with the ocular fluids and tissues. Apart from the process being rudimentary, these lenses are far too thick.

U.S. Patent No. 3,535,386 also proposed the manufacture of cosmetic contact lenses of multi-layer structure, in which covering of the color layer with a polymerizable liquid materiel is resorted to. As indicated in US Patent No. 4,668,240 this type of multi-layer lenses are inconveniently thick and furthermore, due to the layers' defoliation or delamination, leave the color layer exposed.

According to the above mentioned US Patents, the materials that make up the contact lenses are hydrophilic polymers, with little reticulation and derived from the polymerization of vinylic monomers (especially acrylic and/or methacrylic esters). Different variations have been also proposed in this aspect, based on the application of other polymerized materials, such as polyurethane, mentioned in US Patents No. 3,786,034, 3,821,136 and 4,359,558.

U.S. Patent No. 4,668,240 (vide supra), described and claims a method to

produce durable colored contact lenses of great flexibility (as far as it refers to the possibilities of obtaining various colors) transparent or opaque, hydrophilic or flexible, and of thicknesses similar to those of the conventional contact lenses. The method covered by this U.S. Patent comprises partially covering a polymeric contact lens with colored material, including the color components carried in a polymeric medium, and then binding both polymeric matrixes, through covalent links produced between compatible and reactable groups, necessarily present in both polymers, and optionally, also in the color components, with the condition that at least one of said reactive groups, is an oxirane or isocyanate group. Said reactable groups are  $-COOH$ ,  $OH$  and  $-NH_2$  or  $-NH$ -alkyl groups. As examples of monomers including said groups, mention is made of various acrylic monomers, such as methacrylic acid and hydroxymethyl or hydroxyethyl, aminoalkyl or glyceryl esters of monomers copolymerizable with the above mentioned, such as N-vinyl-2-pyrrolidone, vinyl ethers (e.g. vinyl ethyl ether) and alkyl esters of acrylic or methacrylic acid. As it follows from the above stated, the latter patent has its operative limitations and complications, derived from the essential interaction among the reactive groups, which demands complex formulations and costly checking during the industrial process.

The present invention provides, on the contrary, new reaction mechanisms, of greater versatility than those of all the previous ones and a simple and economical practical industrial application.

According to the present invention, there is provided a method for the preparation of lacquers or varnishes for coating contact lenses. The method of the invention comprise the steps of:

a) prepolymerizing by heat or under UV radiation of 375 to 429 nm wavelength a mixture of:

60 to 80 wt.% of N-vinyl-2-pyrrolidone or methyl methacrylate,

4 to 12 wt.% of 2-hydroxyethyl methacrylate or methyl methacrylate,

0.3 to 1 wt.% of a cross-linking agent,

up to 13 wt.% of cyclohexyl methacrylate or acrylate,

8 to 15 wt.% of glycidyl acrylate or methacrylate,

up to 1 wt.% acrylic or methacrylic acid, and

0.1 to 0.5 wt.% of a thermoinitiator or UV photoinitiator of polymerization,

under stirring and at ambient temperature, during a period of time sufficient to form an oily mass, which when heat or radiation is turned off and is rapidly cooled in a  $-30^{\circ}\text{C}$  to  $40^{\circ}\text{C}$  bath, changes into a gel storable at a temperature ranging from  $-10^{\circ}\text{C}$  to  $-25^{\circ}\text{C}$ ;

b) extracting free monomers from said gel until a malleable paste is formed;

c) allowing the paste to settle at ambient temperature so that it may lose, by exudation, any remaining free monomers;

d) dissolving the paste in a non-prepolymerized mixture of monomers defined in step (a) at a temperature not higher than ambient temperature, then filtering and recovering a transparent, colorless and curable lacquer; and

e) optionally, pigmenting the lacquer obtained in step (d) by admixing micronized pigments.

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When the prepolymerization of the monomer mixture in step (a) is carried out by heat, the thermoinitiator is preferably selected from the group consisting of benzoyl peroxide, LUPERSOL 256, (trade mark of a Pennwalt Corp. product), USP 245 (a registered product of Witco Corp.), and azobisisobutyronitrile.

Examples of suitable cross-linking agents which may be used including diallyl maleate, allyl methacrylate, ethyleneglycol diacrylate or dimeth-acrylate, trimethylol propane dimethacrylate, and tri or tetraethylene glycol dimethacrylate, and mixtures thereof. Preferably, use is made of 0.15 to 0.50 wt.% of ethyleneglycol dimethacrylate and 0.15 to 0.50 wt.% of allyl methacrylate.

with the above described method, pigmented or colorless lacquers or varnishes, storable during periods of up to 6 months (at low temperatures, for instance  $-10^{\circ}/-20^{\circ}\text{C}$ ) with no unfavorable changes and consequently, ready to be used, are obtained.

As already pointed out, the lacquers are curable by catalysis, for which reason incorporation of appropriate polymerization catalysts is required prior to their application. For instance, LUPERSOL 256 (trade mark of a Pennwalt Corp. product) or USP 245 (a registered product of Witco Corp.) in a proportion of 0.2 to 1 wt.% with respect to the mass of pigmented lacquer.

The pigmented or colorless inks or lacquers obtained with the method herein described, may be applied over any prepolymerized surface, cellulosic substratum, etc. This means that the formulation of the substratum to

be covered with the ink of the present innovation has no critical importance. It is considered that in this particular aspect of the lacquers as here described, a very important part is played by the reactivity of the glycidyl component whose oxirane (or epoxy) groups react with hydroxyl or amino groups of the polymeric substratum, remaining the colored or colorless layer fixed by means of covalent links of well known chemical stability.

Various cross-linking agents may be used. The preferred ones are diallyl maleate, ethyleneglyucol dimethacrylate, trimethylol propane dimethacrylate and tri or tetra-ethylene glycol dimethacrylate and mixtures thereof.

As possible polymerization catalysts, benzoin, diisopropylxanthogendisulfide (DIPROXID\* R of INC Pharmaceutical), and DAROCUR\* R (Merck), etc., may be mentioned among others.

The operations from a) to e) may be immediately carried out successively or by steps. It is possible, for instance to prepare a relatively large mass of the material to be prepolymerized (monomer mixture: HEMA and N-vinyl-2-pyrrolidone, cross-linker and the glycidyl component), which is stable when stored at 18° to 20°C, to be used later on (in only one batch or in several fractions), the catalytic component being subsequently incorporated and proceeding then to the mass irradiation (under magnetic or mechanic stirring) with UV (an appropriate UV source are the actinic tubes Phillips ILA 20W 05).

This prepolymerization operation is carried out at ambient temperature between 15 and 20°C and it continues until the mass gets a consistency or viscosity that indicates an appropriate polymerization degree. A lapse of

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\* Trade-mark

time of 60 to 90 minutes is generally sufficient to reach such polymerization degree, shown by an evident thickening of the mass, that acquires consistency and oily dripping. At this point the polymerization progress is stopped by turning off the UV and cooling the container in a bath of  $-30^{\circ}$  to  $-40^{\circ}$  C (refrigerated acetone or alcohol bath), while stirring is continued. The resulting mass has a gel consistency, storable at low temperatures ( $-10^{\circ}$  to  $-25^{\circ}$ C), or ready to be immediately processed.

Stage b) above corresponds to the formation of a paste with the prepolymer formulated in stage a). If the gel has been kept at  $-10^{\circ}$  to  $-25^{\circ}$ C, it is left to acquire ambient temperature and then treated by any means known in the art, for a time necessary to extract the free monomers it might contain. The chosen treatment is maintained until all the gel has been transformed into an easily malleable paste, also storable at low temperatures.

As already stated, stage c) consists in leaving the paste to settle at ambient temperature in order that the remainder of free monomers that it might have retained, may be lost by exudation.

Stage d) consists in the preparation of the transparent varnish or lacquer and it implies dissolving the paste obtained in stage c) in established ponderal relations (according to the desired fluidity), with the mixture of monomers reticulants and binder without prepolymerization formulated in stage a). The transparent varnish is generally prepared with 60 parts in weight of the settled paste, and 40 ponderal parts of said monomers mixture. This operation is carried out at a temperature not exceeding ambient temperature, for instance with a cutting blades mixer, checking the temperature and cooling if necessary. It is desirable to leave the solution to

settle one or two days so that it may age and clarify, proceeding then to screen or sieve filtering. This product, storable at low temperatures (-15°/-20°C) is a transparent lacquer or varnish ready to be immediately used or left to age as indicated above.

The final stage e) refers to the preparation of a pigmented ink or lacquer, by mixing the transparent varnish with a pigment or mixture of micronized pigments.

The quantity of pigment obviously depends on the covering power of the chosen pigment and the intensity of the color desired. The mixture is then processed very conveniently in a ball mill or tumbling device. Lacquers storable at -15°/20°C during periods of up to six months, with no noticeable changes, are obtained.

It is thus possible to obtain "type" or "mother" pigmented lacquers of each color, of which, according to requirements, fractions of constant composition and characteristics may be taken ensuring in this manner the obtention of colors with constant shade and intensity.

Although the pigmented or colorless lacquers or varnished obtained with the method herein described, may be used in all the conventional color application or coating techniques: brush, offset printing, aspersion, etc., the preferred method is the offset tampographic printing (offset pad printing) as mentioned in Argentine Patent Applications 301,045, 308,046 and 311,845. This also implies that the printing may be made over the surface of the finished lens or at any prior stage in its production, in conventional "sandwich" or on any stratum of the lens body, or on intermediary dies.

Prior to applying the pigmented varnish on the transparent contact lens, it is activated by adding an appropriate polymerization catalyst for thermal polymerization such as USP 245 or LUPERSOL 256 (vide supra). It is desirable to deionize the transparent lenses (to eliminate the static electricity) prior to coloring. Once the the coloring process is completed, the compound is baked at 100° to 110°C during 10 to 12 hours, and in the case of hydrophilic lenses, they are hydrated according to the conventional practice or as most convenient to the constituent material.

As a reference, examples of the preparation of polymerisable formulations for stage a) of the method under the present invention are included:

#### Example 1

-	N-vinyl-2-pyrrolidone	73.9%
-	2-Hydroxyethyl methacrylate	12%
-	Monomethyl methacrylate	13%
-	Methacrylic Acid	0.50%
-	Allyl methacrylate	0.30%
-	Diallyl maleate	0.30%

9 % of glycidyl acrylate and 0.16% of DIPROXID are added as catalysts to

#### Example 2

-	N-vinyl-2-pyrrolidone	67.18%
-	2-Hydroxyethyl methacrylate	20%
-	Cyclohexyl methacrylate	11.81%
-	Allyl methacrylate	0.45%
-	Ethyleneglycol dimethacrylate	0.45%

11% of glycidyl acrylate and 0.16% of DIPROXIDE are added as catalysts to

this mixture.

**Example 3**

- Methyl methacrylate	98.90%
- Methacrylic acid	0.50%
- Allyl methacrylate	0.30%
- Diallyl maleate	0.30%

14% of glycidyl acrylate and 0.20% of Diproxid as catalyzer is added to this mixture.

The lacquer formulations to obtain the most common colors are as follows:

**Example 4****Blue color**

Lacquer	60.66%
White	14.70%
Blue	8.08%
Red	1.97% (in drops)
Monomer	16.50%

**Example 5****Violet color**

Lacquer	51.43%
Violet	2.86%
White	28.56%
Black	8.57%
Monomer	8.57%

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**Example 6****Green color**

Lacquer	73.61%
Green	2.71%
Yellow	1.24%
Black	2.51%
White	9.70%
Monomer	10.23%

**Example 7****Hazel color**

Lacquer	49.88%
Brown	4.16%
Yellow	11.40%
White	14.61%
Monomer	19.95%

The pigments used in the preparation of the colored lacquers are well known and their names are the following:

**Green Hostaperm 86**

Cu phthalocyanine	CI 74265
	Green Pigment

**Blue Hostaperm A2R**

Stable modification of the Cu phthalocyanine	CI 74160
	Blue pigment 15:1

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**Violet Hostaperm Special**

Dioxazine pigment

CI 51319

Violet pigment 13

**Yellow Hostaperm HAG**Monoazoic pigment of the  
benzimidazolone range

CI 13980

**Brown Hostaperm HFL (Hazelperm-Braun HFL)**

Benzimidazolone pigment

CI 13980

Brown Pigment 32

Solid white (TCO<sub>2</sub> PV-R-01 Hoechst)

As it may be noticed, the outstanding advantages of the present invention are:

- durability of the lens and color layer binding;
- simplicity in the formulation and storage of the colored or colorless lacquer and its intermediary preparations;
- versatility of the colored or colorless lacquer, that may be applied regardless of the constituent chemical groups of the substratum to be colored or covered;
- remarkable reduction of production costs.

The embodiments of the invention, in which an exclusive property or privilege is claimed are defined as follows:

1. A method for the preparation of lacquers or varnishes for coating contact lenses, comprising the steps of:

a) prepolymerizing by heat or under UV radiation of 375 to 429 nm wavelength a mixture of:

60 to 80 wt.% of N-vinyl-2-pyrrolidone or methyl methacrylate,

4 to 12 wt.% of 2-hydroxyethyl methacrylate or methyl methacrylate,

0.3 to 1 wt.% of a cross-linking agent,

up to 13 wt.% of cyclohexyl methacrylate or acrylate,

8 to 15 wt.% of glycidyl acrylate or methacrylate,

up to 1 wt.% acrylic or methacrylic acid, and

0.1 to 0.5 wt.% of a thermoinitiator or UV photoinitiator of polymerization,

under stirring and at ambient temperature, during a period of time sufficient to form an oily mass, which when heat or radiation is turned off and is rapidly cooled in a  $-30^{\circ}\text{C}$  to  $40^{\circ}\text{C}$  bath, changes into a gel storable at a temperature ranging from  $-10^{\circ}\text{C}$  to  $-25^{\circ}\text{C}$ ;

b) extracting free monomers from said gel until a malleable paste is formed;

c) allowing the paste to settle at ambient temperature so that it may lose, by exudation, any remaining free monomers;

d) dissolving the paste in a non-prepolymerized mixture of monomers defined in step (a) at a temperature not higher than ambient temperature,

then filtering and recovering a transparent, colorless and curable lacquer; and

e) optionally, pigmenting the lacquer obtained in step (d) by admixing micronized pigments.

2. A method according to claim 1, wherein in step (a) the monomer mixture comprises 64 to 92 wt.% of monomethyl methacrylate.

3. A method according to claim 1 or 2, wherein the prepolymerization of the monomer mixture is carried out by heat and wherein the thermoinitiator is selected from the group consisting of benzoyl peroxide, LUPERSOL 256, USP 245, and azobisisobutyronitrile.

4. A method according to claim 1 or 2, wherein the prepolymerization of the monomer mixture is carried out under UV radiation of 375 to 420 nm wavelength, and wherein the UV photoinitiator is diisopropylxanthogendisulfide.

5. A method according to any one of claims 1 to 4, wherein the cross-linking agent is selected from the group consisting of diallyl maleate, allyl methacrylate, ethyleneglycol diacrylate or dimethacrylate, trimethylol propane dimethacrylate, and tri or tetraethylene glycol dimethacrylate and mixtures thereof.

6. A method according to claim 5, wherein 0.15 to 0.50 wt.% of ethyleneglycol dimethacrylate and 0.15 to 0.50 wt.% of allyl methacrylate are used.

7. A method according to any one of claims 1, 2, 4, 5 and 6, wherein the prepolymerization of the monomer mixture is carried out under UV radiation of

375 to 420 nm wavelength, and wherein the UV photoinitiator is benzoin or DAROCUR.

8. A method according to claim 1, wherein the monomer mixture comprises 60 to 80 wt.% of N-vinyl-2-pyrrolidone, 4 to 10 wt.% of 2-hydroxyethyl methacrylate, 0.30 wt.% of ethyleneglycol dimethacrylate, 0.30 wt.% of diallyl maleate and 12 wt.% of glycidyl acrylate.

9. A method according to any one of claims 1 to 8, further including the step of applying the lacquer or varnish as a layer over any compatible surface that warrants a solidarity of the binding between layer and substratum.

10. A hydrophilic, flexible and gas permeable contact lens coated with a lacquer or varnish produced by a method as defined in any one of claims 1 to 8.