

COMPOSITION WHICH IS USEFUL FOR OBTAINING
A MATT OR SATIN COATING, USE OF THIS COMPOSITION
AND COATING THUS OBTAINED

The present invention relates to a novel
5 family of compositions containing masked isocyanates
and polyols. The invention relates more particularly to
powders, including mixtures of powders, and to their
use, especially in the form of one-shot powder, in
coatings by means of powders.

10 For reasons associated with protection of the
environment and safety at work, it is increasingly
sought to eliminate the use of solvents in coating
techniques and particularly paint. More particularly,
reducing VOCs (Volatile Organic Compounds) is an
15 increasingly current preoccupation in the paints and
varnishes industry. With this aim, the development of
products with higher solids contents makes it possible
to decrease the amounts of solvents required to achieve
the application viscosity, and thus to reduce the
20 solvents evaporated during drying of the film of paint.

Another alternative is to use products in
aqueous phase in which the water has replaced the
organic solvents as the agent carrying the organic
binder. However, a small amount of organic solvents is
25 required to use and form the film of paint.
Furthermore, they give rise to water-soluble residues
which may be tricky and expensive to process.

In this context, coating techniques using

powders are increasingly being developed. A few details of this technique should be given herein in order to gain a better understanding of the present invention. The technique uses a very finely powdered material for which air acts as a vector.

In general, an electrostatic charge of several kilovolts applied between a gun and the article to be painted allows the coating precursor powder, which will be sprayed by the applicator gun, to be attracted and retained.

Firing of the article between 150 and 200°C then allows melting, spreading and then crosslinking of the paint powder (paint is considered the ultimate example for coatings) in order to obtain a uniform and homogeneous layer of the coating.

This technique is non-polluting and has an application yield of close to 100% by virtue of the possibility of recycling the unused powder.

Among the families of products which may be used in this field, mention should be made of those which are the subject of the following summary:

The majority of the market is occupied by so-called "epoxy-polyester hybrid" powder paints, followed by polyesters and polyurethanes, and then so-called "epoxy" powders.

In order to obtain good quality strength on exteriors (in particular with respect to UV radiation and moisture), it is essential to use coatings based on

TGIC-polyester or polyurethane which, alone, make it possible to achieve the required levels of performance.

The coating powders may be in several finishes (surface aspect, colour, gloss, etc.).

5 The technique used to achieve these effects is different for conventional liquid paints and powder paints.

 When it is desired to modify the gloss, the addition of some fillers such as silicas, carbonates of
10 calcium or barytas makes it possible to reduce the gloss in a range from 50 to 90%, but matt finishes cannot be obtained.

 In the present invention, a hardened, smooth or structured coating which, when applied to a metal
15 support, have a coefficient of reflection which is at most equal to about 50% at a 60°C angle of incidence is defined as a matt or satin system.

 However, the systems which are the most difficult to obtain correspond to coatings which are
20 quite clearly matt, that is to say having a gloss of less than about 30% for a 60°C angle of incidence or less than about 40% at an 85°C angle of incidence.

 One of the techniques most commonly used in order to obtain matt finishes consists in combining
25 compounds with very different reactivities.

 This is achieved by mixing paint powders having short and long gel times. In this way, microscopic heterogeneity will be obtained at the

surface of the coating, thus creating the desired matt effect.

Other techniques make it possible to reduce the gloss of the paints. They consist in using
5 additives or waxes but, on the one hand, they are not sufficient by themselves and, on the other hand, when they are used alone, they generally have reproducibility problems and/or mechanical properties that are really quite insufficient, and/or do not allow
10 them to be used externally on account of their yellowing or the deterioration of the film due to bad weather.

The system most commonly used externally is that known under the name dry-blend, according to which
15 low gloss is obtained by blending extruded and ground powder paints which each have a very different reactivity. Besides the fact that this system is time-consuming and that it involves the manufacture (extrusion, grinding, blending) of several paints, it
20 exhibits a reduced uniformity of the degree of gloss desired, thereby requiring more steps than usual and involving additional costs.

The compounds obtained from the crosslinking reactions should also not be harmful either to human or
25 animal health or to the environment.

For further details regarding the techniques of powder painting, reference may be made to the following books:

→ P. Grandou and P. Pastour: Peintures et Vernis [Paints and Varnishes]:

- I les constituants [constituents]
- II techniques et industries [techniques and industries]; published by Hermann;

5

→ R Lambourne:

Paints and Surface Coatings. Theory and practice; published by Halsted Press;

→ Powder Coating. The Complete Finisher

10

Handbook; the Powder Coating Institute;

→ Myers and Long:

Treatise on Coatings, 5 volumes; published by Marcel Dekker.

Accordingly, one of the aims of the present invention is to provide a composition which makes it possible to obtain coatings by the so-called powder technique.

One of the aims of the present invention is to provide a composition which makes it possible to obtain coatings with good resistance to bad weather.

One of the aims of the present invention is to provide a composition which makes it possible to obtain matt and/or satin coatings.

One of the aims of the present invention is to provide a composition of the above type which is easy to use.

These aims and others which will appear hereinbelow [lacuna] by means of a composition which

contains, for successive or simultaneous addition:

- an isocyanate which is at least partially masked, having a glass transition temperature (sometimes denoted by the abbreviation Tg) of at least about 20°C, advantageously of at least 40°C, and a degree of liberation (with respect to the masking agent) at 120°C of not more than 5%;
- a polyol having the following characteristics:
 - a glass transition temperature (sometimes denoted by the abbreviation Tg) which is at least equal to about 40°C, advantageously at least equal to about 50°C;
 - a hydroxyl number at least equal to about 10 mg/g, advantageously at least equal to about 15 mg/g;
 - an average molecular mass Mn at least equal to about 1000, advantageously to 2000 g/mol.

(In the present description, the term "about" is used to emphasize the fact that the value is rounded up and that, when the figure(s) furthest to the right of a number are zeros, these zeros are positional zeros and not significant figures unless, of course, otherwise stated).

It is preferable for the masking group to bear the labile hydrogen which reacts with the isocyanate function via an oxygen to give the sequence -NH-CO-O- (i.e. $R-NCO + H_2O- \rightarrow R-NH-CO-O-$).

5 According to the present invention, the isocyanate is advantageously masked with at least one masking group bearing at least one function derived from acid functions and especially acid and ester functions. The masking may be mixed and may involve
10 several masking groups.

In the structure of the isocyanate(s), it is desirable for the part of the skeleton connecting two isocyanate functions to contain at least one polymethylene chain $(CH_2)_\pi$ where π represents an integer
15 from two to 10, advantageously from 4 to 8. This preference acts on the matt effect and on the mechanical performance levels. When there are several chains, they may be similar or different. In addition, it is desirable for at least one and preferably all of
20 these chains to be free to rotate and thus be exocyclic.

The degree of liberation is quantified by the octanol test (see below).

According to the present invention, the
25 masked isocyanate, pure or as a mixture, is derived from a polyisocyanate, that is to say having at least two isocyanate functions, advantageously more than two (possibility of fractional values since it is generally

a mixture of more or less condensed oligomers), this polyisocyanate itself usually being derived from a precondensation or a prepolymerization of unitary diisocyanate (occasionally referred to in the present description as "monomer").

In general, the average molecular mass of these prepolymers or of these precondensates is at most equal to 2000 (one significant figure), more commonly to 1000 (one significant figure, preferably two).

Thus, among the polyisocyanates used for the invention, mention may be made of those of the biuret type and those whose di- or trimerization reaction has led to four-, five- or six-membered rings. Among the six-membered rings, mention may be made of the isocyanuric rings obtained from a homo- or a hetero-trimerization of various diisocyanates alone, with other isocyanate(s) [mono-, di- or polyisocyanate(s)] or with carbon dioxide, in which case a nitrogen of the isocyanuric ring is replaced by an oxygen. Oligomers containing isocyanuric rings are preferred.

The preferred polyisocyanates are those which have at least one aliphatic isocyanate function. In other words, at least one isocyanate function masked according to the invention is connected to the skeleton via an sp^3 -type carbon advantageously bearing one hydrogen atom, preferably two. It is desirable for the said sp^3 -type carbon itself to be borne by an sp^3 -type

carbon and advantageously carry one, preferably two, hydrogen atoms, in order to prevent the isocyanate function considered from being in a neopentyl position. In other words, it is recommended to choose as monomer
5 (which, in general, bear two isocyanate functions) at least one compound which bears at least one aliphatic function which is neither secondary nor tertiary nor neopentyl.

In the case of the mixture obtained from
10 several (in general two) types of monomers, it is preferable for this or these monomers, which satisfy the above conditions and/or (advantageously "and") the condition regarding the presence of a polymethylene chain $(CH_2)_n$, to represent at least 1/3, advantageously
15 1/2, preferably 2/3 of the masked isocyanate functions. Thus, in the course of the study according to the present invention, excellent results were obtained with mixtures containing two-thirds HMDT (hexamethylene diisocyanate "trimer") with IPDI or IPDT (IPDI
20 "trimer"), the two being masked according to the invention (nBDI, norbornane diisocyanate, and its trimer are similar).

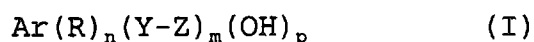
Obviously, the case in which all of the isocyanates are aliphatic and moreover satisfy the
25 above criterion is preferred.

The agents leading to the masking groups characteristic of the invention are advantageously chosen from those which are obtained from the

condensation of an aromatic derivative hydroxylated on the ring and bearing a function chosen from nitrile and, preferably, carbonyl functions with an isocyanate. It goes without saying that the condensation takes
 5 place on the phenol function.

Among the members of that family, it is convenient to choose those for which an apparent melting point may be determined, this measurement being carried out at room temperature (20°C). This melting
 10 point should be at least equal to 30°C (one significant figure), advantageously to 50°C.

It is preferable to choose from among those of formula (I):



15 where Ar is an aromatic residue on which is grafted n substituents R, m polar functions Z chosen from nitriles and carbonyl groups, and p hydroxyl functions.

Values of n, m and p are such that the sum
 20 $n + m + p$ is at most equal to the number of substitutable chain members; p is advantageously at most equal to 2 and is preferably equal to 1.

Advantageously, m is at most equal to two and is preferably equal to 1.

25 Advantageously, n is at most equal to 3, preferably chosen from zero, one and two, more preferably equal to zero.

R represents substituents that are inert

towards the masking reaction and, in general, corresponds to hydrocarbon chains, usually alkyl chains in the etymological sense of the term, namely an alcohol whose hydroxyl function has been removed.

5 Two vicinal substituents R may be connected together to form a ring which may, for example, be aromatic.

 Z is advantageously chosen from groups having a carbonyl function. Among these functions, mention
10 should be made of alkoxycarbonyl functions (or, in other words, ester functions), the amide function, the ketone function with the preferred condition that there are no acidic hydrogens [in other words the function advantageously does not bear hydrogen or, if it does,
15 the corresponding pKa is at least equal to about 20 (one significant figure, preferably two) and more preferably at least equal to about 25] α to the carbonyl function (ester, ketone or amide). Thus, the preferred amides (including lactam or even urea) are
20 advantageously substituted, preferably, sufficiently for there to be no hydrogens on the nitrogen of the amide function or such that there are no reactive hydrogens.

 Where Y is chosen from divalent groups,
25 advantageously -O-, -S-, NR'- and -CR'R"- with R' and R" chosen from hydrocarbon radicals, advantageously alkyls, of 1 to 6 carbon atoms, advantageously of 1 to 4 carbon atoms, preferably methyl, more preferably

hydrogen; and preferably Y represents a single bond.

It is preferable for the polar function(s) Z (generally chosen from the nitrile function and/or the carbonyl functions) not to be vicinal to the group Z as, for example, in salicylic acid.

The aromatic residue Ar consists of one or more hetero- or homocyclic, advantageously fused rings. It is preferable for Ar not to contain more than two rings and preferably not more than one ring.

The aromatic residue Ar may consist of one or more heterocyclic or homocyclic rings, usually homocyclic on account of their ease of access. The value of six-membered heterocycles, which have a liberation temperature very much lower than that of the corresponding homocycles, should, however, be pointed out.

It is desirable for the total number of carbons in the aromatic derivative hydroxylated on the ring to be at most equal to 20, preferably equal to 10 (one significant figure).

This ring is advantageously 6-membered, the ring units consisting of carbon or nitrogen with the number of substituents required for the valency of these atoms.

Among the acids and derivatives, especially esters, which give the most satisfactory results, mention should be made of acids grafted onto a benzene ring or onto pyridine rings. Thus, meta-hydroxybenzoic

acid and, especially, para-hydroxybenzoic acid, and their derivatives, give good results.

As has been mentioned above, it is possible to provide several groups (preferably two for economic reasons) masking the isocyanate functions. This diversity may be achieved by mixing various masked (in general with only one group) compounds or preferably by coreaction. These masking groups may all be as defined above or only some of them may correspond to this definition. In the latter case, it is preferable for those (that is to say the sum of those) which bear a carbonyl (ester or acid) function advantageously to correspond to the above formula (I) and to correspond to at least about 10% (expressed as blocked isocyanate function), advantageously to about 20%, preferably to 1/3.

The presence of a carboxylic acid function (-COOH) and in particular of a carboxylic acid function grafted directly onto an aromatic ring, advantageously a benzene ring, makes it possible, on the one hand, to increase the melting point of the blocked isocyanate and, on the other hand, to increase significantly the matt effect of the coating after crosslinking (for example the final paint). However, it is preferable, in order to retain the excellent mechanical properties of the system according to the present invention, for the amount of acid function present (in terms of equivalents) to be at most equal to about 9/10,

advantageously to about 4/5, preferably to 2/3 of the masked isocyanate functions. The beneficial effects of the acid functions on the matt effect and on the glass transition temperature (T_g) already become apparent
5 from about 10%, but it is desirable to reach a proportion of at least 20%. In addition, at this concentration level and beyond, the acid functions facilitate the appearance of irregularities which give a so-called "structured" appearance. The melting point
10 and the glass transition temperature (T_g) continually overlap with the acid content up to 100%.

One of the most advantageous of the uses consists in using isocyanates which are at least partially masked by a compound bearing an acid
15 function, advantageously by a compound of formula I where Z is an acid function. It is recommended that the isocyanate then be masked by a group other than that bearing the acid function, and that the acid function of the masking system be between 90 and 10% (expressed
20 as blocked isocyanate function). The other masking agent or agents may be either masking agents which are known per se (which satisfy the liberation temperature and the unmasking constraints specified in the present description), or an ester corresponding to formula I.
25 The latter alternative form is preferred. For the synthesis of these compounds, reference may be made to the general procedures of patent application No. EP 0,680 984 A which gives good results for the operation

of (optionally partial) masking by a compound of formula I.

When only one masking agent is used, it is desirable for this to be a compound according to formula I where Z is ester, with the preferences indicated in patent application No. EP 0,680 984 A, page 2, lines 41 to 50.

As has already been mentioned according to the present invention, it is preferable for the melting point of the compound or of the mixture of compounds obtained to have an apparent melting point which is at least equal to 30°C, preferably 50°C.

It is also preferable for the glass transition temperature to be at least equal to 20°C, advantageously to 40°C.

It is preferable to choose the compounds according to the present invention such that they react completely with a primary alcohol at 250°C in less than half an hour.

The reaction is considered to be complete if it proceeds to 90% or more.

As has been mentioned above, the isocyanates for which the invention is most advantageous are those whose nitrogen atom is linked to a carbon of sp^3 hybridization, and more particularly aliphatic isocyanates, and especially polymethylene diisocyanates (for example TMDI tetramethylene diisocyanate and HMDI [hexamethylene diisocyanate = $OCN-(CH_2)_6-NCO$]) and their

various condensation derivatives (biuret, etc.) and di- and trimerization derivatives (in the field under consideration the term trimer refers to mixtures derived from the formation of isocyanuric rings from
5 three isocyanate functions; in fact, along with the actual trimer, there are heavier products derived from the trimerization).

According to the present invention, it is desirable and sometimes necessary for the percentage of
10 residual free isocyanate function to be at most equal to 5%, advantageously to 3%, preferably to 1%. The highest melting points or glass transition temperatures are obtained with percentages not exceeding 0.5%. The contents of aromatic derivatives hydroxylated on the
15 ring are also advantageously low, that is to say at most equal to 5%, advantageously to 3%, preferably to 1%.

If reference is made to the compounds which may be used as polyols for the composition according to
20 the invention, those which make it possible most easily to obtain powder paints or powder varnishes of low gloss are hydroxylated acrylic resins and/or linear or branched, hydroxylated, saturated or unsaturated polyesters having an appropriate molecular weight and
25 capable of being crosslinked by a reaction with an isocyanate prepolymer (that is to say an isocyanate which is at least partially masked according to the invention).

The said prepolymer is provided with masked (or blocked) active functions and it is activated thermally by liberation of the blocking agent, by exchanging the isocyanate groups which react with the hydroxyl groups of the binder, in the presence or
5 absence of catalysts.

This system makes it possible to obtain powder paints having a suitable viscosity on melting and a glass transition temperature above 40°C, thereby
10 entailing chemical and physical stability during storage.

The possible functionality of the carboxyl, which defines the molecular weight of the polymer, thus allows a double-crosslinking with aromatic or aliphatic epoxy resins and/or hydroxyalkylamides.
15

The said excess of acidic groups is determined by its acid number, expressed in milligrams of potassium hydroxide required to neutralize the free acidity of one gram of polyol (occasionally referred to
20 as "resin").

The hydroxyl number corresponds to the milligrams of potassium hydroxide required per gram of resin in order to neutralize the excess acetic acid liberated during acetylation (with acetic anhydride)
25 of the hydroxylated polymer. For further details, reference may be made to standard ASTM-E222.

The hydroxyl number of the polymer may range between 10 and 350 mg KOH/g, preferably between 15

and 80. The acid number is at most equal to about 20 mg KOH/g, advantageously at most 15 mg KOH/g: it is also advantageously at least 2 mg KOH/g, preferably at least 4 mg KOH/g. A good choice
5 consists in taking hydroxylated polymers whose acid number is preferably between 3 and 15 mg KOH/g.

The number-average molecular weight, $\overline{M}_n$ of the binder or hydroxylated polymer of the present
10 invention ranges between 2000 and 15,000 g/mol. The molecular weight is determined by gel permeation chromatography (GPC). The technique uses, as gels, two polystyrene gels (Ultrastyrigel® at 10^4 and 500 Å), THF as solvent and sulphur as standards.

15 It is desirable for the degree of branching (that is to say the average number of free OH functions per molecule) to be between 2 and 4, advantageously between 2.5 and 3.

The matt effect increases as the branching
20 increases. Branching may be obtained using polyols with functionality of more than two (in general triols) or polyacids (often used in the form of anhydride in order to reduce the amount of water released during the reaction) with a functionality of more than two. The
25 latter case is preferred for the matt effect. In particular, trimellitic acid, especially in the form of anhydride, is very favourable.

In the case of the use of hydroxylated

polyesters for the present invention, the product of the esterification of one or more aliphatic, aromatic or cycloaliphatic di- or polycarboxylic acids or anhydrides or their methyl esters, which contain 2 to 5 36 carbon atoms, is used.

For example, mention may be made of adipic acid, succinic acid, sebacic acid, suberic acid, azelaic acid, decanedicarboxylic acid, glutaric acid, terephthalic acid, isophthalic acid, phthalic acid or 10 anhydride, naphthalenedicarboxylic acid, hexahydrophthalic acid or anhydride, 1,4-cyclohexanedicarboxylic acid, dimerized fatty acids and trimellitic anhydride.

The molecular weight of the polymer may be 15 adjusted by adding aliphatic or aromatic monocarboxylic acids, or their methyl esters, having 2 to 18 carbon atoms.

The percentage of the acid(s) or anhydride(s) described above within the polymer mixture ranges 20 between 20 and 70%, preferably between 30 and 60%, taken individually or mixed.

If the polymer of the present invention is unsaturated, di- or polycarboxylic acids or anhydrides unsaturated as olefins, such as maleic acid or 25 anhydride, tetrahydrophthalic acid or anhydride, fumaric acid, hexachloroendomethylenetetrahydrophthalic acid or anhydride, methylmaleic acid, itaconic acid or derivatives of dicyclopentadiene, or of methylmaleic,

itaconic, maleic or fumaric acid, are used.

Among the polyhydroxylated alcohols which are useful for synthesizing the polyester are: ethylene glycol, 1,2- or 1,3-propylene glycol, 2-methylpropane-
5 diol, diethylene glycol, dipropylene glycol, 1,4-butanediol, 2,3-butylene glycol, 1,6-hexanediol, 1,5-pentanediol, neopentyl glycol, cyclohexane-dimethanol, triethylene glycol, neopentyl glycol hydroxypivalate, tetraethylene glycol, polyethylene
10 glycol, polypropylene glycol, dibutylene glycol or polyethylene glycols, trimethylpentanediol, butylethylpropanediol, glycerol, trimethylolpropane, hexanetriol, pentaerythritol, sorbitol, trimethylolethane and tris(2-hydroxyethyl)
15 isocyanurate. The percentage of these may range between 10 and 60%, preferably between 10 and 50%.

For the preparation of the polyesters, and in particular during creation or conversion of the ester bond, it is indicated to use catalysts which are known
20 "per se" for the esterification; these catalysts, which may be found in the final composition, may be used alone or as a mixture. Among the catalysts which may be used in the context of the present invention, mention should be made more particularly of those based on
25 protic acid (especially those which are organic) or based on Lewis acid, which is advantageously organic. More specifically, among the protic organic acids, mention may be made of sulphonic acids, the most common

of which are paratoluenesulphonic acid and methanesulphonic acid. Among the Lewis acids, mention should be made of those based on titanium, such as titanium tetrachloride, tetra-n-butyl titanate, isopropyl titanate, tetrakis(2-ethylhexyl) titanate, titanium acetylacetonate, stearyl titanate, nonyl titanate or cetyl titanate, those based on vanadium such as isopropyl vanadate or n-butyl vanadate, those based on zirconium such as zirconium tetrachloride, n-propyl zirconate or n-butyl zirconate, those based on tin such as anhydrous or hydrated tin chlorides, dibutyltin oxide, tin octanoate, butyltin hexanoate, tin oxalate, monobutyltin oxide, monobutylchlorotin dihydroxide, dibutyltin dilaurate, dibutyltin diacetate and monobutyltin tris(2-ethylhexanoate).

The use of the above catalysts is particularly advantageous in the case of saturated hydroxylated polyesters, and in a percentage by mass advantageously between 1/2 and 2% (by mass) relative to the saturated hydroxylated ester.

Addition of the compounds of the above types makes it possible in particular to reduce the manufacturing time and the emission of volatile compounds, and allows optimization of the final colour of these polyols which is particularly suitable for the present invention.

In the case where a methyl ester (of di- or polycarboxylic acids) is used at the start, it is very

desirable to use those of the above catalysts which are known for giving satisfactory catalysis of the transesterification, or to introduce other catalysts which are known to do this, for example zinc
5 carboxylates, antimony trioxide or any other catalyst known to those skilled in the art in the technical field of condensation. The amounts to be used are advantageously between 1/2 and 1% (by weight) of the initial charge.

10 Besides working in an inert atmosphere, in order to improve the polymer or to protect it from coloration during the esterification process, it is preferable to add antioxidant additives such as triphenyl phosphite, tris(nonylphenyl) phosphite,
15 stearyl pentaerythritol diphosphite or equivalents thereof. These compounds are preferably used in an amount at least equal to 5 per thousand and at most equal to 15 per thousand.

In order to obtain the polyester mentioned
20 above, techniques which are known per se are used. The usual reaction conditions may be mentioned, namely:

- final temperature between about 200°C and 260°C,
- absolute pressure between 5 hectopascals and
25 800 kilopascals.

The acid number and the hydroxyl number should be controlled; the alkalinity is adjusted to the point which makes it possible to obtain the best

properties of covering of the polyurethane. Thus, before unloading, in principle in a refrigerated chamber, catalysts, antioxidants and any additive required for the final application are incorporated.

5 The polyesters used for the present invention have a glass transition temperature (T_g) of between 40 and 80°C, preferably between 50 and 70°C, in order to give the system the stability required during storage. It is possible to use mixtures of amorphous and
10 crystalline polyesters, the appropriate proportions of which must allow both good chemical and good physical stability. The T_g of the polymer is determined by calorimetry by differential analysis (DSC).

 In the present invention, in the case where
15 hydroxylated acrylic polymers are used, only one binder is used, the T_g being between 40 and 100°C, or alternatively mixtures are used comprising 0 to 30% of an acrylic polymer, the T_g being between -20 and 50°C, and 70 and 100% of a hydroxylated acrylic polymer, the
20 T_g being between 40 and 100°C. With the said mixture, the system may be treated easily and have good stability during storage, as well as good chemical and mechanical properties.

 The hydroxylated acrylic polymers may be
25 obtained by reacting alpha,beta-unsaturated ethylene monomers, in particular vinylaromatic monomers and esters of alpha,beta-unsaturated ethylenecarboxylic acids. Mention may be made, for example, of styrene and

its derivatives, such as methylstyrene or chlorostyrene; in the case of products for exteriors, they are present in amounts of between 5 and 54%, preferably between 10 and 25% of the monomers as a whole. Amounts less than 5% may affect the corrosion resistance.

Among the alpha, beta-unsaturated ethylene acid esters, mention may be made of acrylic and methacrylic acid esters such as methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, dodecyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate and lauryl methacrylate. Preferably, the unsaturated esters are present in an amount of between 5 and 8%, and correspond to a mixture of esters of alkyl having 1 to 3 carbon atoms and 4 to 20 carbon atoms, for example a mixture of methyl methacrylate and butyl acrylate.

The hydroxyl functionality of the acrylic polymer is imparted by the copolymerization of monomers having hydroxyl groups, such as hydroxyethyl methacrylate and acrylate, and hydroxypropyl acrylate and methacrylate, in amounts of between 5 and 80%, this percentage, which relates to the monomers as a whole, being necessary in order to obtain the hydroxyl number indicated.

The acrylic polymer may have a certain acid number, normally less than 15, derived from the

addition of acrylic acid, methacrylic acid, itaconic acid or fumaric acid and/or of maleic acid or anhydride.

In order to prepare the said acrylic
5 polymers, the various monomers are mixed together and are reacted by free-radical polymerization. Among the initiators which may be used, mention may be made in particular of benzoyl peroxide, tert-butyl hydroperoxide, di-tert-butyl peroxide and
10 azobisisobutyronitrile. Chain-transfer agents such as mercaptopropionic acid, dodecyl and lauryl mercaptan may be used to adjust the molecular weight. The polymerization is carried out in solution, using a solvent in which the monomers are soluble, such as
15 toluene, xylene, butyl acetate and propylene glycol methyl ether acetate, inter alia. Once the polymerization is complete, the reaction mixture is evaporated, under vacuum, in order to remove the organic solvent and to recover the solid polymer. The
20 residual content of solvents or volatile compounds should be less than 0.5%.

Admittedly, when the hydroxylated acrylic polymers are used in accordance with the conditions described above, satisfactory crosslinking with a
25 prepolymer containing isocyanate functions masked according to the present invention is obtained with the desired matt effect, but the mechanical properties remain insufficient for uses subjected to bad weather.

Thus, it is preferred to use polyisocyanate and saturated polyester systems.

The acid number which the polymer of the present invention has makes it possible to react the
5 carboxyl groups with aliphatic, aromatic and/or beta-hydroxyalkylamide polyepoxides, and double-crosslinking is thus obtained.

As has been mentioned previously, the esterification catalysts may be found in the final
10 polyester and may act as matt-effect agent. In order to improve the reproducibility of this effect and to allow the polyacrylic di- or polyalcohols to benefit therefrom, it is preferable, so as to have a good matt effect, to verify the presence of and, if necessary, to
15 add an esterification (including transesterification) catalyst.

A binder catalyst content at least equal to 0.5%, advantageously to 1% and preferably to 2% should be ensured. It is preferable for the content not to
20 exceed 5%, advantageously 3%, preferably 2% by mass. As most catalysts are based on elements of metallic nature, it may be more practical to express this characteristic in terms of atomic equivalents. In this case, it is expressed that a content at least equal to
25 0.003 equivalent per kg mass (of binder), advantageously 0.005, preferably 0.01 equivalent, should be achieved, and it is preferable for the content not to exceed, on a mass basis, 0.3 equivalent,

advantageously 0.2 equivalent, preferably 0.1 equivalent per kg mass (of binder).

The esterification catalysts which give the best matt effect are catalysts having one, preferably
5 both, of the following characteristics:

- a low liposolubility,
- a solid, advantageously crystalline form.

As regards the low liposolubility, it should be mentioned that these preferred catalysts are only
10 sparingly soluble or are insoluble in the media (chlorobenzene + octanol) of the octanol test (see below).

In general, in order to satisfy these conditions, it is preferable to choose inorganic salts
15 [having a catalytic activity] and/or organic salts (including salts derived from hydrocarbons, such as, for example, those corresponding to the "anion" CH_3CH_2^- , although they are not the most advantageous), such as sulphonate, carboxylate, acetylacetonate,
20 phosphate, phosphonate or phosphinate, which have few methylene or methyl units, advantageously on average not more than 3 per anion (for example the malonic dianion $[\text{OOC}-\text{CH}_2-\text{COO}^-]$ has 1/2 methylene per anion), preferably not more than 2, more preferably not more
25 than 1, and even zero.

As regards the solid form, it is preferable for the melting point to be above that of the mixture, particularly by extrusion.

Among the catalysts which give particularly good results, mention should be made of tin II salts such as pyruvate, oxalate, halide and in particular chloride (which also have the advantage of giving a so-called structured surface).

This catalyst which promotes the matt effect may be introduced at various steps in the preparation of the powder paint, in particular during the blending before the final extrusion or during the preceding operations, in particular in the polyols after the condensation.

The use of these polyols containing at least one of the above catalysts is particularly favourable for carrying out the present invention (in order to calculate the concentrations, the above data may be used for the binder, given that the polyol represents 80% of the binder). Polyols which act as vector product for the catalyst may also be used, thus facilitating its packaging in the final mixture. In this case, the concentration by mass is higher than the values given in the above binder and may reach 25 or even 50%.

The binder of the present invention makes it possible to obtain matt (low gloss), smooth, structured, textured paints and other effects such as the shot-blasted effect, using the additives, fillers, pigments and manufacturing processes known to those familiar with the manufacture of powder coatings. The presence of (matt-effect) waxes in the coating

composition makes it possible to improve the matt effect, but this promotes the formation of microcraters, which should be avoided in certain uses of paint. Given the above, a person skilled in the art will choose whether or not to use these waxes.

These waxes, which are known per se, may be chosen from polyethylene oxides, and are added in a proportion ranging from 0 to 5% relative to the binder (by mass).

They may also be chosen from mixtures of polyethylene oxides of the above type and fluoro-, advantageously perfluoro-hydrocarbons and, in particular, tetrafluoroethene polymers (PTFE). In the case of fluorohydrocarbons, it is preferable not to substantially exceed 1%. They are generally used at a content of greater than 0.1% relative to the binder.

The fillers and pigments together may reach $\frac{2}{3}$ of the mass of the binder.

In the formulation of paints, the appropriate pigments which make it possible to obtain the desired colour should be present, it being possible for these pigments to range between 1 and about 50% by weight of the total of the powder paint. Fillers may thus be used in the formulation in amounts of between 5 and 40%.

Among the pigments, special mention should be made of titanium dioxide, since this pigment may have a neutral role or may promote the matt appearance, depending on the pretreatment chosen. It was seen that

titanium oxides which have undergone a silica (and possibly alumina) treatment significantly increased the matt effect, the one having the most pronounced effect being that sold under the name Titafran RL68 (now sold
5 under the name rhodo RL68).

Titanium dioxides treated with zirconium oxide have little influence on the matt effect.

A person skilled in the art can thus easily modify the satin or matt nature by acting on the
10 titanium dioxide used.

The paint or the varnishes according to the present invention may contain the various types of additives, which are known per se, such as degassing agents, levelling agents, antioxidants and UV absorbers
15 (anti-UV agents). They may also contain the various matt-effect adjuvants known to improve this effect.

Thus, as recommended degassing agents, mention may be made of benzoin, present in particular in an amount of between 0.5 and 3%, which makes it
20 possible to release the volatile compounds from the film during hardening and to prevent defects such as the formation of craters or pits.

The spreading additives recommended are acrylic polymers, fluoro polymers or polymeric
25 siloxanes, in amounts of between 0.5 and 5% added directly as a "master batch" into suitable polymers or absorbed onto silica.

In order to improve the exterior strength and

the resistance to overfiring or to hardening in ovens with direct gas injection, it is recommended to add to the formulations UV-absorbing compositions and/or antioxidants of the primary and/or secondary type, of the phenolic type or alkyl/aryl phosphites. The said additives may be present in the formulation in an amount of between 0.5 and 2% of the paint as a whole.

In order to reduce the hardening (crosslinking) temperature, catalysts for formation of urethane, such as DBTDL (dibutyltin dilaurate) may be added to the formulation, directly into the premix or as a master batch.

The matt powder paints which form the subject of the present invention may advantageously be manufactured by melt-blending the compounds of the formulation. Firstly, they are preblended in a blender and are then melted, they are homogenized and are dispersed in an extruder which has one or more screws.

It is desirable for the mixing, blending and extrusion temperature to be at most equal to about 130°C, advantageously to about 110°C, preferably to 100°C (3 significant figures). It is desirable for the extrusion temperature to be at least equal to about 60°C, advantageously to about 70°C, preferably around 80 - 90°C. The extruded material obtained is left to cool and is passed through a mill until a paint having the desired particle size is obtained (in general d_{90} is at most equal to about 200 micrometres, advantageously

100 micrometres (2 significant figures) and d_{10} at least equal to about 20 micrometres, advantageously about 50 micrometres) in order to apply it to metal supports such as steel, aluminium or other alloys, glass,
5 plastic or wood.

The ratio between the polyol(s) and the isocyanate(s) is defined by the deblocking stoichiometry. The amount of isocyanate stoichiometrically required to react with all of the
10 free hydroxyls is generally chosen, with a tolerance of 20%, advantageously of 10%, preferably of 5%. As it is preferable to have an excess of isocyanate, slightly offset ranges are preferred. In other words, the amount of isocyanate to be added is advantageously at least
15 equal to about 90% and at most equal to about 120% of the stoichiometric amount; preferably, it is at least equal to 95% and at most equal to about 110% of the stoichiometric amount; the most common and thus the most desirable range is at least equal to 100% (3
20 significant figures) and at most equal to 105% of the stoichiometric amount. When systems having a high proportion of free acid (for example at least 2/3 of the masked isocyanate functions, see above) are used, it may be envisaged to increase the ratio between
25 isocyanate and hydroxyl function from 10 to 30 points (%) approximately relative to the above values.

The powder obtained may be applied with an electrostatic gun or by a fluid bed. The preferred

application of the present invention is that carried out with the Corona-charge and Corona-effect electrostatic gun or by friction (triboelectric).

The substrate onto which the paint is
5 applied, mainly steel or aluminium, may or may not be preheated before the application. Once applied, the powder is melted and hardened in an oven for 10 minutes to 2 hours at a temperature of between 140 and 220°C depending on whether or not the system is catalysed,
10 generally for 10 to 30 minutes at a temperature ranging from 180°C to 220°C.

Bearing in mind the preceding text, a person skilled in the art will adapt the firing by recalling that increasing the firing temperature makes it
15 possible to decrease the firing time, and vice versa.

The present invention will be better understood with the aid of the illustrative examples which follow, in which the various exterior/interior matt paint systems are compared, in order to indicate
20 the favourable points of the system proposed.

OCTANOL TEST - definitions

- "liberation" (or : this is the lowest
 "deblocking") temperature at which the
 temperature masking agent of the masked
 isocyanate is 9/10
 (mathematically rounded-up)
 displaced by a primary
 monoalcohol (the primary
 alcohol is generally octanol)
- 5 shelf life : in order to ensure a good
 shelf life, it is preferable to
 choose masked isocyanate
 functions whose octanol test
 shows a "liberation" at 80°C,
 advantageously at 90°C, which
 is at most equal to 90%.
- reaction progress : the reaction is considered to
 be complete if it proceeds to
 more than 90%.

PROCEDURE

About 5 mmol of protected masked NCO
 equivalent to be evaluated are loaded into a Schott-
 10 type tube with magnetic stirring.

2.5 to 3 ml of 1,2-dichlorobenzene (solvent)
 and the equivalent of 1-octanol (5 mmol, i.e. 0.61 g,
 optionally with the catalyst to be tested with the
 masking group) are added.

The reaction medium is then brought to the test temperature. It is then heated for 6 h at the test temperature, so as to deblock the isocyanate functions and thus make them reactive. Once the reaction is complete, the solvent is removed by distillation under vacuum and the residue is analysed by NMR, mass spectrum and infrared.

From these data, the percentage of masked isocyanate function condensed with the 1-octanol is evaluated.

PRODUCTS USED

The products used in the examples below are often denoted by their trade name. These products are described in technical sheets whose references will be found in the following table:

Trade name	Marketed by	Type of chemical product	Technical sheet reference	Date pub- lished
PT810	Ciba Geigy	glycidyl isocyanurate	37236/f 750.313:15	
BYK-360 P	Byk Chemie GmbH	polyacrylate adsorbed onto silica	SM 18	June 1993
Cerafluor 961	Byk Cera	micronized polyethylene wax	XM 961	Septem- ber 1995

	Trade name	Marketed by	Type of chemical product	Technical sheet reference	Date pub- lished
	DT 3329-1	Ciba Geigy	wax		April 1994
	XB 4957	Ciba Geigy	matt-effect agent	Best. No. 93118	November 1993
	Primid XL 552	EMS	hydroxyalkyl- amide hardener	7.2.1	
5	accelerator DT 3126	Ciba Geigy		38037/F 900.110/20	January 1990
	Reafree 3300	Resisa	saturated hydroxylated polyester	3300/950119	January 1996
	Reafree 7000	Resisa	saturated hydroxylated polyester*	7000/960725	July 1996
	Reafree 4001	Resisa	saturated carboxylated polyester	4001/960329	March 1996
10	Reafree 4401	Resisa	saturated carboxylated polyester	107370/ 960221	February 1996

Trade name	Marketed by	Type of chemical product	Technical sheet reference	Date pub- lished
Reafree 8580	Resisa	saturated carboxylated polyester	107240/ 930309	March 1993
Reafree 8180	Resisa	saturated carboxylated polyester	8180/960521	May 1996

*The batch used for Examples g and f of this
hydroxylated polyester contained an appreciable
5 proportion of residual esterification catalyst

Definitions of abbreviations and margins of uncertainty

IPDT = IPDI (isophorone diisocyanate) trimer

HDT = HDI (hexamethylene diisocyanate) trimer

MPHB indicates that the blocking is performed with
10 methyl para-hydroxybenzoate

PHBA indicates that the blocking is performed with
para-hydroxybenzoic acid

The glosses are measured with an uncertainty of 5%
(absolute)

15 Examples A to E and G are comparative.

EXAMPLE A

Two white pigmented weatherproof powder paint
formulations using polyesters of different reactivity
and of different ratio with TGIC were obtained as
20 follows:

	Trade name	Powder composition No. 1	Powder composition No. 2
	Constituents	Parts by mass (grams)	
	90/10 carboxylated polyester	Reafree 4001 540.0	-
5	96/4 carboxylated polyester	Reafree 4401 -	576.0
	Triglycidyl isocyanurate	Araldite PT810 (Ciba) 60.0	24.0
10	Benzoin	3.0	3.0
	Spreading agent	Byk 360P from Byk-Chemie 9.0	9.0
	Titanium dioxide	RL 60 from Rhône Poulenc 300.0	300.0

15 The components of each of the paints are
 blended in a blender and then homogenized separately
 and by melting in a single-screw extruder of the Büss
 PCS-30 type, at a temperature between 80 and 120°C. The
 extruded material is left to cool and it is flaked on
 20 cooling rollers, ground and classified according to the
 desired shape. Once the two paints have been obtained,

they are blended 1/1 in a high-speed blender. Once the homogenization has been carried out, the resulting powder of the mixture is applied electrostatically to steel or aluminium plates. They are hardened for 12 to 5 15 minutes at 200°C, the temperature of the substrate. Once the hardening has been carried out, the gloss (matt effect) of the samples applied is observed. The results and the properties are summarized in Table 1. The problem of the said system is that it requires the 10 manufacture of two paints and the mixing of ground powders (dry-blend). This system has the drawback of poor reproducibility and small variations lead to variations in the degree of gloss.

EXAMPLE B

15 White pigmented weatherproof Primid-based paint. Dry-blend system, mixing of paints 1 and 2 as in Example A.

	Trade name	Powder composition No. 1	Powder composition No. 2
Constituents		Parts by mass (grams)	
20 95/5 Carboxylated polyester	Reafree 8580	570.0	-
89/11 Carboxylated polyester	Reafree 8180	-	540.0

	Trade name	Powder composition No. 1	Powder composition No. 2
Constituents		Parts by mass (grams)	
Hydroxy-alkylamide crosslinking agent	Primid XL-552 (EMS-Chemie)	30.0	60.0
5 Benzoin		2.0	2.0
Spreading agent	Byk 360-P	6.0	6.0
Titanium dioxide	RL 60 from Rhône Poulenc	390.0	390.0

10 Has the same drawbacks as A.

EXAMPLE C

White pigmented weatherproof TGIC-based paint. Use of a highly acidic matt-effect agent.

	Trade name	Powder composition
Constituents		Parts by mass (grams)
15 96/4 carboxylated polyester	Reafree 4401	540.0
Triglycidyl isocyanurate	Araldite PT810 (Ciba)	91.0

	Trade name	Powder composition
Constituents		Parts by mass (grams)
Matt-effect agent	XB 4957	53.0
Benzoin		2.0
Spreading agent	Byk 360-P	6.0
5 Titanium dioxide	RL 60 from Rhône Poulenc	328.0
Accelerator	DT 3126	6.0

The paint has an excellent matt appearance and low gloss at 60°C and 85°C, but the mechanical properties are entirely unsatisfactory.

EXAMPLE D

White pigmented weatherproof paint based on TGIC (triglycidyl isocyanurate). Use of a matt-effect wax.

	Trade name	Powder composition
		Parts by mass (grams)
15 Constituents		D
96/4 carboxylated polyester	Reafree 4401	583.0

	Trade name	Powder composition
	Triglycidyl isocyanurate	Araldite PT810 (Ciba)
	Matt-effect wax	DT 3329-1
	Benzoin	
5	Spreading agent	Byk 360-P
	Titanium dioxide	RL 60 from Rhône Poulenc
	Accelerator	DT 3126

The matt appearance obtained is unsatisfactory, although the other properties are correct.

EXAMPLE E

White pigmented weatherproof polyurethane paint based on a prepolymer of isophorone diisocyanate masked with ϵ -caprolactam, for use on exteriors.

	Trade name	Powder composition
15	Constituents	Parts by mass (grams)
	Hydroxylated polyester, OH = 40-50	Reafree 3300
		448.2

	Trade name	Powder composition
5	Caprolactam-masked IPDI prepolymer	Vestagon BF-1530 from Hüls 129.8
	Micronized wax	Cerafluor 961 from Byk-Cera 20.0
	Benzoin	3.0
	Spreading agent	Byk 360-P from Byk-Chemie 9.0
	Titanium dioxide	RL 60 from Rhône Poulenc 290.0
	Baryta	100.0

The mechanical properties are acceptable but
 10 the matt effect remains poor.

EXAMPLE F

Matt polyurethane white powder paint for use
 on exteriors.

According to that indicated in the present
 15 invention, the use of a special polyester with the
 isocyanate prepolymer indicated makes it possible to
 obtain matt systems which have good mechanical
 properties and exterior strength.

	Trade name	Powder composition No. 1
Constituents		Parts by mass (grams)
Hydroxylated polyester, OH : 40-50	Reafree 7000	502.0
5 Methyl para-hydroxybenzoate-masked HDI "trimeric" prepolymer	Methyl para-hydroxybenzoate-masked Tolonate® HDT	76.0
10 Micronized wax	Cerefluor (Byk 961)	20.0
Benzoin		3.0
Levelling agent	Byk 360-P	9.0
Titanium dioxide	RL 60 from Rhône Poulenc	290.0
Baryta		100.0

15 The mechanical properties are exceptional
(but this does not emerge in the test since the
conditions do not make it possible to demonstrate them,
the maximum being achieved everywhere) and the matt
effect is good.

20 **EXAMPLE G**

Cross-example in which the ester of Example F
is used with the isocyanate of Example E.

	Trade name	Powder composition No. 1
	Constituents	Parts by mass (grams)
	Hydroxylated polyester, OH : 40-50	448.2
5	Caprolactam-masked IPDI prepolymer	Vestagon BF-1530 from Hüls 129.8
	Micronized wax	Cerafluor 961 from Byk-Cera 20.0
	Benzoin	3.0
10	Spreading agent	Byk 360-P from Byk-Chemie 9.0
	Titanium dioxide	RL 60 from Rhône Poulenc 290.0
	Baryta	100.0

TABLE 1

Paint	Example A	Example B	Example C	Example D	Example E	Example F	Example G
Hardenig	12'200°C	15'200°C	12'200°C	12'200°C	15'200°C	15'200°C	15'200°C
20°C gloss	5.8	9.0	1.9	9.5	52	7.2	24
60°C gloss	26.5	34.3	4.5	42.9	71	29.9	63
85°C gloss	27.8	32.8	15.9	59.8	99	34.4	90
Direct impact (cm)	75	75	20	75	75	75	75
Reverse impact	75	75	0	75	75	75	75
Adhesion	100	100	100	100	100	100	100
Folding (conical mandrel) (%)	100	100	100	100	100	100	100
Resistance to methyl ethyl ketone (butanone) (double passage)	>200	>200	40	>200	>200	>200	>200
Exterior strength	Excellent	Excellent	Good	Excellent	Excellent	Excellent	Excellent

Example H: white paint

MATERIALS			
Reafree 7000	454.0	443.0	453.0
MPHB-masked HDT	121.0		
HDT/IPDT (75/25)		132.0	
MPHB/PHBA-masked HDT (80/20)			122.0
Tin oxalate	3.0	3.0	3.0
Cerafluor 961	20.0	20.0	20.0
White set ABR	100.0	100.0	100.0
Benzoin	3.0	3.0	3.0
Byk 360P	9.0	9.0	9.0
TiO ₂ (RL-68)	290.0	290.0	290.0
TOTAL	1000.00	1000.00	1000.00
Characteristics of the paints after firing			
Substrate	Steel (R-36)		
Firing (Temperature/Time)	200°C 20 m	200°C 20 m	200°C 20 m
Apperance/Layer (microns)	MAT 60	SAT/60	MAT/60
Impact (Direct/Reverse)	45/10	75/35	75/75
Adhesion/Drawing	100/5	100/9.5	100/> 10

Folding	100	100	100
MEK resistance	105	> 200	> 200
20°C gloss	5	6	3
60°C gloss	30	35	15
85°C gloss	50	67	19
Substrate	Steel (R-36)		
Firing (Temperature/Time)	210°C 20 m		
Appearance/Layer (microns)	MAT-SA 60	SAT**/60	MAT/60
Impact (Direct/Reverse)	75/75	75/75	75/75
Adhesion/Drawing	100/> 10	100/> 10	100/> 10
Folding	100	100	100
MEK resistance	> 200	> 200	> 200
20°C gloss	5.7	6.3	2.5
60°C gloss	30	35	15
85°C gloss	55	70	20

** SAT = satin

Example I: White paint

MATERIALS		
Reafree 7000	452.2	451.5
HMDT 35% PHB; 65% MPHB**	122.8	
HMDT 50% PHB; 50% MPHB		123.50
SnC ₂ O ₄	3.0	3.0
Cerafluor 961	20.0	20.0
White set ABR	100.0	100.0
Benzoin	3.0	3.0
Byk 360P	9.0	9.0
TiO ₂ (RL-68)	290.0	290.0
TOTAL	1000.00	1000.00
Substrate	Steel (R-36)	
Firing (Temperature/Time)	200°C 20m	200°C 20 m
Appearance/Layer (microns)	MA-RU 70	MA-RU 70
Impact (Direct/Reverse)	75/75	75/75
Adhesion/Drawing	100/> 10	100/> 10
Folding	100	100
MEK resistance	> 200	> 200
20°C gloss	3.4	2.1
60°C gloss	18.7	7.0

85°C gloss	32.3	9.0
Substrate	Steel (R-36)	
Firing (Temperature/Time)	210°C 20 m	210°C 20 m
Appearance/Layer (microns)	MA-RU 70	MA-RU 70
Impact (Direct/Reverse)	75/75	75/75
Adhesion/Drawing	100/> 10	100/> 10
Folding	100	100
MEK resistance	> 200	> 200
20°C gloss	3.4	2.2
60°C gloss	18.4	7.9
85°C gloss	31.1	10.4

Example J: white paint

MATERIALS			
Reafree 7000	450.0	171	451
Tin oxalate	4	1.4	4
(CaCO ₃)	20.0	8.0	20.0
MPHB-masked HDT	120.0		
MPHB-masked HDT		54.8	
N-hydroxysuccinimide masked HDT			113.0
Cerafluor 961	20.0	8.0	20.0
White set ABR	80.0	36.0	90.0
Benzoin	3.0	1.2	3.0
Byk 360P	9.0	3.6	9.0
TiO ₂ (RL-68)	290.0	116.0	290.0
Millicarb(CaCO ₃)	10.0		
TOTAL	1000.00	400.00	1000.00
CHARACTERISTICS			
Substrate	Steel (R-36)	Steel (R-36)	Steel (R-36)
Firing/Temperature/ Time	210°C 20 m	200°C 20 m	200°C 20 m
Appearance/Layer (microns)	MAT/50	SAT/80	SAT*/70

Impact (Direct/Reverse)	75/75	75/40	75/75
Adhesion/Drawing	100/> 10	100/5.4	100/> 10
Folding	100	0	100
MEK Resistance	> 200	150	> 200
20°C gloss	4	19	18
60°C gloss	23	50.0	55**
85°C gloss	60	71	75

* yellowing

** virtually at the satin limit, see above

Example K: structured matt black paint

MATERIALS	
SnCl ₂	3
Reafree 7000	443.0
Rhodocoat x D2D (MPHB-masked HMDT)	117.00
Dolomie	92.0
White set ABR	298.0
Cerafluor 961	20.0
Byk 360P	9.0
Benzoin	3.0
Raven 1020 (carbon black)	15.0
TOTAL	1000.0
CHARACTERISTICS	
Substrate	
Firing (Temperature/Time)	200°C 20 m
Appearance/Layer (microns)	
Impact (Direct/Reverse)	75/75
Adhesion/Drawing	100
Folding	100
MEK Resistance	100
20°C gloss	1.2
60°C gloss	6.1
85°C gloss	9.5

Example L: matt white paint

MATERIALS	
Reafree 7000	464.0
Tin oxalate	4
Rhodocoat XD2D	120.00
Titafran RL-68	290.0
White set ABR	90.0
Cerafluor 961	20.0
Byk 360P	9.0
Benzoin	3.0
TOTAL	1000.0
Firing (Temperature/Time)	200°C 20 m
Impact (Direct/Reverse)	75/75
Adhesion/Drawing	100
Folding	100
MEK Resistance	> 200
60°C gloss	17.8
85°C gloss	34.4

Example M: colour formulations

MATERIALS	matt red paint	matt brown paint	matt black paint
Reafree 7000	454.0	453.0	451.0
Insoluble catalyser	2	2.6	3
Rhodocoat XD2D	117.0	117.0	117.0
Dolomite	92	92	92
White set ABR	260	264.7	290
Cerafluor 961	20	20.0	20
Byk 360P	9	9.0	9
Benzoin	3	3	3
Raven 1020			15
Bayferrox 130	20.9	12	
Printex V	0.2	2.7	
Cinquasia Violet R RT 887 D	17.6		
Hornachrome yellow GMXH-35-SQ		14.2	
Ti Pure R-960	4.2	9.8	
TOTAL	1000.00	1000.00	1000.00

CHARACTERISTICS			
Substrate			
Firing (Temperature/Time)	200°C 20 m	200°C 20 m	200°C 20m
Appearance/Layer (microns)			
Impact (Direct/Reverse)	75/75	75/75	75/75
Adhesion/Drawing	100	100	100
Folding	100	100	100
MEK Resistance	> 200	> 200	> 200
20°C gloss	3.3	2.8	1.7
60°C gloss	19.7	15.4	11.0
85°C gloss	47.6	35.5	30.0

CLAIMS

1. Composition characterized in that it contains, for successive or simultaneous addition:

→ an isocyanate which is at least partially masked, having a glass transition temperature of at least 20°C, advantageously of at least 40°C, and a degree of liberation (with respect to the masking agent) at 120°C of not more than 5%;

→ a polyol having the following characteristics:

- a glass transition temperature which is at least equal to about 40°C, advantageously at least equal to about 50°C;
- a hydroxyl number at least equal to about 10 mg/g, advantageously at least equal to about 15 mg/g;
- an average molecular mass M_n at least equal to about 1000 g/mol and advantageously to 2000 g/mol.

2. Composition according to Claim 1, characterized in that the isocyanate is advantageously masked by a masking group bearing at least one ester function.

3. Composition according to Claim 1 or 2, characterized in that the hydroxyl number of the said polyol may range between 10 and 350 mg KOH/g, preferably between 15 and 80.



This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

4. Composition according to any one of Claims 1 to 3, characterized in that the acid number is at most equal to 20 mg KOH/g, preferably between 3 and 15 mg KOH/g.

5. Composition according to any one of Claims 1 to 4, characterized in that the average molecular mass $\overline{M_n}$ of the binder or hydroxylated polymer of the present invention ranges between 2000 and 15,000 g/mo.

6. Composition according to any one of Claims 1 to 5, characterized in that the hydroxylated polymer of the present invention has a melting point which is at most equal to about 130°C, advantageously to about 110°C, preferably to 100°C (3 significant figures).

7. Composition according to any one of Claims 1 to 6, characterized in that, after mixing, the composition is in powder form.

8. Composition according to Claim 7, characterized in that the powder has a d_{90} which is at most equal to about 200 micrometres, advantageously 100 micrometres.

9. Composition according to Claim 6 or 8, characterized in that the powder has a d_{10} which is at least equal to about 20 micrometres, advantageously about 50 micrometres.

10. Composition according to any one of Claims 1 to 9, characterized in that it also contains

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

titanium dioxide.

11. Composition according to any one of Claims 1 to 10, characterized in that it also contains a catalyst having one, preferably both, of the following characteristics:

- low liposolubility,
- a solid, advantageously crystalline form.

12. Composition according to any one of Claims 1 to 11, characterized in that it has a particle size, defined by a d_{90} , which is at most equal to about 200 micrometers, advantageously to 100 micrometers (2 significant figures) and a d_{10} which is at least equal to about 20 micrometers, advantageously to about 50 micrometers.

13. Process for preparing compositions according to any one of Claims 1 to 12, characterized in that it includes a step in which the compounds of the formulation are preblended in a blender, after which the polyol and advantageously the other meltable components are melted at a chosen temperature, homogenized and dispersed in an extruder which has one or more screws.

14. Process [lacuna] Claim 13, characterized in that the blending and extrusion temperature is at most equal to about 130°C, advantageously to about 110°C, preferably to about 100°C (3 significant figures).

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

15. Process for preparing compositions according to Claim 10 or 14, characterized in that the extrusion temperature is at least equal to about 60°C, advantageously to about 70°C, preferably around 80-90°C.

16. Process for preparing compositions according to any one of Claims 10 to 15, characterized in that it also includes a cooling step followed by a grinding step in order to obtain a particle size, defined by a d_{90} , which is at most equal to about 200 micrometers, advantageously to 100 micrometers (2 significant figures) and a d_{10} at least equal to about 20 micrometers, advantageously to about 50 micrometers.

17. Use of the composition according to any one of Claims 1 to 16, for coatings and in particular for paint.

18. Coating obtained by the use of the composition according to any one of Claims 1 to 9.

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED