

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 painting techniques. More
particularly, reducing VOCs (Volatile Organic
15 Compounds) is an 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
20 to reduce the 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
25 binder. However, a small amount of organic solvents is
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.

5 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,
10 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 being considered the ultimate
15 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.

20 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
25 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 have several finishes
5 (surface aspect, colour, gloss, etc.).

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
10 addition of fillers such as silicas, carbonates of 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
15 or structured coating which, when applied to a metal support, has 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
20 difficult to obtain correspond to coatings which are 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
25 order to obtain matt finishes consists in combining 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 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 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 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 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 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]
 - 5 - II techniques et industries [techniques and industries]; published by Hermann;
- R Lambourne:
Paints and Surface Coatings. Theory and
10 practice; published by Halsted Press;
- Powder Coating. The Complete Finisher Handbook; the Powder Coating Institute;
- Myers and Long:
Treatise on Coatings, 5 volumes; published by
15 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.

20 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
25 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.

The Applicants filed a European patent application No. 96/401703.2 relating to a composition containing, for successive or simultaneous addition:

- an isocyanate which is at least
5 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 release
10 (with respect to the masking agent) at 120°C of not more than 5%;
- a polyol having the following characteristics:
 - a glass transition temperature
15 (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
20 about 10 mg/g, advantageously at least equal to about 15 mg/g;
 - an average molecular mass Mn at least equal to about 1000 g/mol and advantageously to 2000 g/mol.

25 (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).

This composition already had great advantages
5 over the prior art:

the above aims and others which will become apparent hereinbelow by means of a composition, in particular of the above type, which also comprises at least one, advantageously 2 and preferably three of the
10 following characteristics:

- ⇒ the presence of a carboxylic function, in particular in the form of a mixed masked isocyanate (see below);
- ⇒ the presence of a solid esterification catalyst
15 (see below);
- ⇒ a matt-effect wax (see below).

The carboxylic function is advantageously in intimate mixture with the isocyanate component of the composition. It is even desirable for the carboxylic
20 function to be grafted onto the isocyanate system via an agent bearing both a reactive function (i.e. a function containing a so-called labile hydrogen) with the isocyanate function and a carboxylic function (COOH in salt form or advantageously in free form). It is
25 highly desirable for this agent bearing a carboxylic function to be a masking agent.

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. $R-NCO + HO- \rightarrow R-NH-CO-O-$).

According to the present invention, the
isocyanate is advantageously masked with at least one
5 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
several masking groups.

In the structure of the isocyanate(s), it is
10 desirable, especially for the matt effect, 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 from 2 to 10, advantageously from
4 to 8. This preference acts on the matt effect and on
15 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 these chains to be free to rotate and
thus to be exocyclic.

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

According to the present invention, the
masked isocyanate, pure or as a mixture, is derived
from a polyisocyanate, that is to say a compound having
25 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 a "monomer").

In general, the average molecular mass of
5 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
10 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 heterotrimerization of various diisocyanates alone,
15 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.

20 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 a hydrogen
25 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 carrying, 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 (which, in general, bear two isocyanate functions) at least one compound which bears at least one aliphatic function
5 which is neither secondary nor tertiary nor neopentyl.

In the case of the mixture obtained from 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
10 condition regarding the presence of a polymethylene chain $(CH_2)_n$, to represent at least $1/3$, advantageously $1/2$, 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
15 mixtures containing $2/3$ HMDT (hexamethylene diisocyanate "trimer") with IPDI or IPDT (IPDI "trimer"), the two being masked according to the invention (nBDI, norbornane diisocyanate, and its trimer are similar).

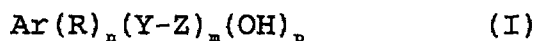
20 Obviously, the case in which all of the isocyanates are aliphatic and moreover satisfy the above criterion is preferred.

The agents leading to the masking group(s) characteristic of the invention are advantageously
25 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 place on the phenol function.

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

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



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

Values of n, m and p are such that the sum $n + m + p$ 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.

20 Advantageously, m is at most equal to 2 and is preferably equal to 1.

Advantageously, n is at most equal to 3, preferably chosen from zero, 1 and 2, and more preferably equal to zero.

25 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.

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

5 Z is advantageously chosen from groups having a carbonyl function. Among these functions, mention should be made of alkoxycarbonyl functions (or, in other words, ester functions), the amide function, the ketone function with the preferred condition that there
10 are no acidic hydrogens [in other words the function advantageously does not bear hydrogen or, if it does, the corresponding pKa is at least equal to about 20 (one significant figure, preferably 2) and more preferably at least equal to about 25] α to the
15 carbonyl function (ester, ketone or amide). Thus, the preferred amides (including lactam or even urea) are advantageously substituted, preferably, sufficiently for there to be no hydrogens on the nitrogen of the amide function or such that there are no reactive
20 hydrogens.

Where Y is chosen from divalent groups, 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
25 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.

5 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 hetero- or homocyclic rings, usually homocyclic on account of their ease of access. The value of six-
10 membered heterocycles, which have a release 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
15 ring to be at most equal to 20, preferably to 10 (one significant figure).

This ring is advantageously six-membered, the ring units consisting of carbon or nitrogen with the number of substituents required for the valency of
20 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 even onto pyridine rings. Thus, meta-
25 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 masking group) compounds or
5 preferably by coreaction. These masking groups may all be as defined above or only some of them may correspond to such definitions. 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
10 advantageously to correspond to the above formula (I) and to correspond to at least about 10% (expressed as isocyanate function), advantageously to about 20%, preferably to 1/3.

The presence of a carboxylic acid function
15 (-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
20 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
25 equivalents) to be at most equal to about 9/10, advantageously to about 4/5, preferably to 2/3, more preferably one third of the isocyanate functions. When the carboxylic functions are borne by agents which are

not released under the curing conditions, it is preferable, in order to retain the crosslinking power, for the amount of acid borne by agents which are not released to be not more than 1/2, advantageously 1/3 of
5 the total amount of isocyanate functions (free, masked and linked to a non-releasable masking agent [cf. aminocaproic acid of the examples])).

The beneficial effects of the acid functions on the matt effect and on the glass transition
10 temperature (T_g) already become apparent from 5% and are very noticeable from 10%, but it is desirable to reach a proportion of at least 20% in order to obtain an effect close to the inflexion of the curve. In addition, at this concentration level and beyond, the
15 acid functions facilitate the appearance of irregularities which give a so-called "structured" appearance. The melting point and the glass transition temperature (T_g) continually overlap with the acid content up to 100%.

20 When an ester/acid couple is involved, and in particular when an alkyl hydroxybenzoate/hydroxybenzoic acid couple is involved, a good compromise between the matt effect and the various usual properties is already obtained in the region of a 90/10 molar ratio; i.e.
25 about 9/10 of ester and about 1/10 of acid.

The presence of acid functions to a proportion of about 1/10, in particular carboxylic, allows good catalysis of the crosslinking.

The effects outlined above for isocyanate compounds masked with two or more masking agents can be obtained either by a mixture of two or more isocyanates masked with a single masking agent or with isocyanates masked simultaneously or successively with two or more masking agents. The latter case gives better results correlated to the existence of so-called mixed molecules, i.e. molecules in which at least one of the isocyanate functions is masked with an agent bearing an acid function, and at least one of the isocyanate functions is masked with an agent not bearing an acid function. The positive effects of the presence of these so-called mixed molecules become apparent once they correspond to (i.e. once they bear) about 5% of the isocyanate functions, advantageously 10%.

Thus, one of the most advantageous of the uses consists in using isocyanates which are at least partially masked with a compound bearing an acid function, advantageously with a compound of formula I where Z is an acid function. It is recommended that the isocyanate then be masked with a group other than that bearing the acid function, and that the acid function of the masking system be between 90 and 10% (expressed as blocked isocyanate function). The other masking agent or agents may be either masking agents which are known per se (which satisfy the release temperature and the unmasking constraints specified in the present description), or an ester corresponding to formula I.

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 with a compound of formula I.

It may be recalled here that the masking agents most commonly used are those cited by M. Wicks in his article "blocked isocyanates" [Progress in Organic Coatings (1975), Vol. 3, p. 73] - their deblocking temperature are advantageously greater than 90°C.

the masking agents can be divided into three groups:

- ⇒ those in which the labile hydrogen is borne by a chalcogen;
- ⇒ those in which the labile hydrogen is borne by a nitrogen;
- ⇒ those in which the labile hydrogen is borne by carbon.

Among those in which the labile hydrogen is borne by a chalcogen (preferably light chalcogens, i.e. sulphur and oxygen), the ones especially used are those in which the chalcogen is an oxygen; among the latter, mention may be made in particular of:

- products containing an >N-OH sequence such as, for example, oximes (= N-OH) or hydroxy imides ($[-CO-]_xN-OH$); and

- phenols (in the broad sense), especially those in which the aromatic ring is electron-poor, such as the hydroxybenzoates described in the present invention;

5 mention may also be made of the compounds described in patent application EP-A-661,278.

 Among those in which the labile hydrogen is borne by a nitrogen, mention may be made in particular of:

- 10 - monosubstituted amides, and in particular lactams (the one most commonly used is caprolactam);
- imides ($[-CO-]_2N-H$), especially cyclic imides such as succinimide;
- unsaturated nitrogenous heterocycles, which are
15 five-membered in particular (advantageously containing double unsaturation), preferably comprising at least two hetero atoms (preferably nitrogen); among the latter, mention may be made of diazoles (such as glyoxalines and pyrazoles),
20 triazoles or even tetrazoles;
- mention may also be made of the compounds described in patent application EP-A-661,278.

 The masking agents in which the labile hydrogen is borne by carbon are essentially compounds
25 of malonic nature, i.e. a radical $RCH<$ bearing two electron-withdrawing groups (such as carbonyl, nitrile, R_f or [perfluoroalkyl]).

The masking agents (alone or as a mixture) above can be used to implement the present invention provided that the following two constraints are satisfied:

- 5 - they are combined with an agent
 (advantageously a masking agent) bearing
 carboxylic function(s) and a function which
 is reactive (and which can advantageously
 be released on curing) with the isocyanate
10 functions (with the preferences indicated
 in the present description);
- compounds derived from the reaction
 between the isocyanate, on the one hand,
 and the masking agent and the agent bearing
15 carboxylic function(s), on the other hand,
 have the required glass transition
 temperature (T_g) (and melting point).

One of the advantages of using a carboxylic group according to the present invention lies in the
20 fact that it makes it possible to use masking groups
which, without the presence of a carboxylic group,
would not have a sufficient melting point or glass
transition temperature (T_g) for use in powder
application. This is the case in particular for
25 triazoles, which, when unsubstituted (each of the
isomers alone or as a mixture in any proportion of the
isomers), are particularly cost-effective.

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.

5 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.

10 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
15 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
20 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
25 [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 three isocyanate functions; in fact, along with the actual trimer, there are heavier products derived from the trimerization).

5 According to the present invention, it is desirable and sometimes necessary for the percentage of residual free isocyanate function (therefore expressed in equivalents) attached to a skeleton comprising an exocyclic polymethylene chain (see above) to be at most
10 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 derivative hydroxylated on the ring are also advantageously low,
15 that is to say at most equal to 5%, advantageously to 3%, preferably to 1%.

 However, up to a mass content of 1/3, the presence in the said isocyanate of unmasked trimers of cycloaliphatic monomers such as IPDT or nBDT have a
20 favourable effect on the glass transition temperature (T_g) and does not in any way impede the production of high-quality coating. Such compositions can be readily obtained by mixing the unmasked trimer in the molten masked compound.

25 If reference is made to the compounds which may be used as polyols for the composition according to 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 capable of being crosslinked by a reaction with an
5 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
10 thermally by release of the blocking agent, by exchanging the isocyanate groups which react with the hydroxyl groups of the binder, in the presence or absence of catalysts.

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

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

The said excess of acid groups is determined by its acid number, expressed in milligrams of
25 potassium hydroxide required to neutralize the free acidity of one gram of polyol (occasionally referred to 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 released during acetylation (with acetic anhydride) of the hydroxylated polymer. For further
5 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;
10 it is also advantageously at least 2 mg KOH/g, preferably at least 4 mg KOH/g. A good choice consists in taking hydroxylated polymers whose acid number is preferably between 3 and 15 mg KOH/g.

15 The number-average molecular weight, $\overline{M}_n$, of the binder or hydroxylated polymer of the present 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
20 polystyrene gels (Ultrastyrigel® at 10^4 and 500 Å), THF as solvent and sulphur as standards.

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
25 between 2.5 and 3.

The matt effect increases as the branching increases. Branching may be obtained using polyols with a functionality of more than 2 (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 2; the 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 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 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 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 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 anhydride, tetrahydrophthalic acid or anhydride,
5 fumaric acid, hexachloroendomethylenetetrahydrophthalic acid or anhydride, methylmaleic acid, itaconic acid or derivatives of dicyclopentadiene, or of methylmaleic, itaconic, maleic or fumaric acid.

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

For the preparation of the polyesters, and in
25 particular during creation or conversion of the ester bond, it is indicated to use catalysts which are known "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 protic acid (especially those which are organic) or
5 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
10 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,
15 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 octoate, butyltin hexanoate, tin
20 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 hydroxylated
25 saturated polyesters, and in a percentage by mass advantageously between 1/2 and 2% 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 coloration of these polyols which is particularly
5 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
10 transesterification, or to introduce other catalysts which are known to do this, for example zinc 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
15 advantageously between 1/2 and 1% (by mass) of the initial charge.

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

In order to obtain the polyester mentioned 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 800 kilopascals.

5 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
10 chamber, catalysts, antioxidants and any additive required for the final application are incorporated.

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

 For the present invention, in the case where hydroxylated acrylic polymers are used, only one binder is used, the Tg being between 40 and 100°C, or alternatively mixtures are used comprising 0 to 30% of
25 an acrylic polymer, the Tg being between -20 and 50°C, and 70 to 100% of a hydroxylated acrylic polymer, the Tg 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
5 obtained by reacting α,β -unsaturated ethylene monomers, in particular vinylaromatic monomers and esters of α,β -unsaturated ethylenecarboxylic acids. Mention may be made, for example, of styrene and its derivatives, such as methylstyrene or chlorostyrene; in the case of
10 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 α,β -unsaturated ethylene acid
15 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
20 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.

25 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.

5 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.

10 In order to prepare the said acrylic 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
15 hydroperoxide, di-tert-butyl peroxide and azobis(isobutyronitrile). 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
20 solvent in which the monomers are soluble, such as 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
25 organic solvent and to recover the solid polymer. The residual content of solvents or volatile compounds should be less than 0.5%.

When the hydroxylated acrylic polymers are

used in accordance with the conditions described above,
satisfactory crosslinking with a prepolymer containing
isocyanate functions masked according to the present
invention is indeed obtained with the desired matt
5 effect, but the mechanical properties remain
insufficient for uses subject to bad weather. Thus, it
is preferred to use polyisocyanate and saturated
polyester systems.

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

As has been mentioned previously, the
15 esterification catalysts may be found in the final
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
20 effect, to verify the presence of and, if necessary, to
add an esterification (including transesterification)
catalyst.

A binder catalyst content at least equal to
0.5%, advantageously to 1% and preferably to 2% should
25 be ensured, and it is preferable for the content not to
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 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 both, of the following characteristics:

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

As regards the low liposolubility, it should be mentioned that these preferred catalysts are only 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 [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, 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 than 1, and even zero.

5 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 capable of giving very good results, mention may be made of those which are
10 renowned for catalysing allophanation reactions; another category of catalyst which moreover broadly covers that of allophanation catalysts are catalysts of the carboxylic acid isocyanate reaction.

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

 Among the catalysts which give particularly
20 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).

 Surprisingly, the catalysts which can be used
25 as catalysts for the masking reaction can promote the appearance of the matt effect (or satin effect). Thus, as catalysts which promote the matt effect, mention may also be made of organic bases whose basic function is

borne by a nitrogen or phosphorus atom, nitrogen being preferred. It is desirable for the basic atom not to bear hydrogen. The basicity is at least equal to that of pyridine rings (for example pyridine itself,
5 picolines or quinoline). The preferred bases are phosphines or, preferably, tertiary amines. The tertiary amines can contain from three up to about 50 carbon atoms per basic function (it is recalled that it is more practical for there to be only one per
10 molecule). Heavy amines, in particular fatty amines, have a favourable effect on the appearance of the painted surface, but the effect on the matt effect is slightly weaker.

Amines also have a favourable effect on the
15 mechanical properties, which indicates a catalysis of the crosslinking in powder phase.

It is, admittedly, preferable for the organic bases to be relatively non-volatile per se (b.p. at least equal to 80°C, advantageously 100°C, preferably
20 200°C), but under the conditions for crosslinking powders, the observation of the low volatility is not very restricting and is, in particular, easily achieved provided that there are free acid functions in the binder in an amount at least equal to the amount of
25 base (expressed in equivalents). If not, it is possible to envisage using heavier bases, i.e. bases whose molecular mass is at least equal to 100, advantageously 180, preferably fatty bases, i.e. bases whose molecular

mass is greater than 250. The organic bases can be pure or in a mixture. The amines can comprise other functions and in particular functions corresponding to amino acid functions and cyclic ether functions such as
5 N-methylmorpholine, or otherwise. These other functions are advantageously in a form which does not react with the isocyanate functions. In order to obtain a strong matt effect, it is desirable for the amount of amine to be at least equal to about 1% (in equivalents),
10 advantageously 2%, preferably 3% of the masked isocyanate functions in the powder. The amines can be used alone or in combination with the preferred metal catalysts mentioned above.

This (these) catalyst(s) which promote the
15 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.

20 The use of these polyols containing at least one of the above catalysts is particularly favourable for implementing the present invention (in order to calculate the concentrations, the above data may be used for the binder, given that the polyol represents
25 80% of the binder). Part of the 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,
5 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
10 composition makes it possible to improve the matt effect, but this promotes the formation of microcraters, which should be avoided in certain uses of paints. Given the above, a person skilled in the art will choose whether or not to use these waxes.

15 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
20 polyethylene oxides of the above type and fluoro-, advantageously perfluorohydrocarbons and, in particular, tetrafluoroethylene polymers (PTFE). In the case of fluorohydrocarbons, it is preferable not to substantially exceed 1%; they are generally used at a
25 content of greater than 0.1% relative to the binder.

The fillers and pigments together may reach 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
5 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
10 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.

Titanium dioxides treated with zirconium
15 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 titanium dioxide used.

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

25 Thus, as a recommended degassing agent, mention may be made of benzoin, present in particular in an amount of between 0.5 and 3%, which makes it possible to release the volatile compounds from the

film during hardening and to prevent defects such as the formation of craters or pits.

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

In order to improve the exterior strength and the resistance to overfiring or to hardening in ovens
10 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
15 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
20 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
25 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 5 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 to 100 micrometres (2 significant figures) and d_{10} at 10 least equal to about 20 micrometres, advantageously to about 50 micrometres) in order to apply it to metal supports such as steel, aluminium or other alloys, glass, plastic or wood.

The ratio between the polyol(s) and the 15 isocyanate(s) is defined by the deblocking stoichiometry. The amount of isocyanate stoichiometrically required to react with all of the free hydroxyls is generally chosen, with a tolerance of 20%, advantageously of 10%, preferably of 5%. As it is 20 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 equal to about 90% and at most equal to about 120% of the stoichiometric amount; preferably, it is at least 25 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% (three 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
5 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
10 out with the Corona-charge and Corona-effect electrostatic gun or by friction (triboelectric).

The substrate onto which the paint is applied, mainly steel or aluminium, may or may not be preheated before the application. Once applied, the
15 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, generally for 10 to 30 minutes at a temperature ranging from 180°C to 220°C.

20 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 possible to decrease the firing time, and vice versa.

One of the advantages of the present
25 invention lies in the fact that it is able to obtain deep matt effects without it being necessary to use compounds containing at least one amide function substituted with an alkyl which itself bears an alcohol

function beta to the nitrogen [these products are often sold under the name Primid[®] and usually correspond to the diamidation of a diacid (for example adipic acid, malonic acid, succinic acid, glutaric acid, etc. or a mixture thereof) with diethanolamine]. Admittedly, it is possible to use them, but their addition provides very little additional matt effect. Thus, it is possible in particular to use only a small amount (not more than 3% by mass of the coating, advantageously not more than 2%, preferably not more than 1%) or better still not to add any at all.

Thus, according to the present invention, it is possible to obtain coatings which have a very mildly alveolar structure. The alveolae are few in number and represent a volume which is small enough for the mechanical properties not to be adversely affected thereby, but in the region of the surface they are converted into craters which are invisible without magnification and give rise to waves whose size (height difference) is of the same order of magnitude as the wavelengths of the visible spectrum.

More specifically, the compositions according to the present invention make it possible to obtain matt or satin coatings which advantageously have, on average on a normal section at the surface, waves with a height difference of from 0.2 to 5 μm (micrometres), preferably from 0.4 to 3 μm (micrometres) and in the most favourable cases from about 1 to 3 μm

(micrometres).

The statistical density is advantageously of the order of from 5 to 500 "waves" per millimetre and preferably from about 10 to about 100 "waves" per
5 millimetre.

Some of these waves can correspond (and this improves the quality of the matt effect) (viewed from above) to circles (resembling, under very high magnification, highly flattened [lunar] craters). [The
10 craters with a diameter of less than 0.2 μm (micrometre) and greater than 10 μm (micrometre) are not taken into consideration].

In general, these craters represent from 1/20 to 1/3 of the area.

15 Half of the area, advantageously 2/3 and preferably three quarters corresponds to craters whose diameter is at least equal to 1, advantageously to 2 μm (micrometre) and at most equal to 6 μm , preferably 5 μm (micrometre).

20 One of the characteristics of the compositions according to the present invention is to release, under the crosslinking conditions, a small amount of carbon dioxide which gives rise to the alveolae, craters and/or waves and the matt effect.

25 The alveolae can be clearly seen with an electron microscope.

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 the favourable points of the system proposed.

5 **OCTANOL TEST - definitions**

"release" (or : this is the lowest
"deblocking") temperature at which the
temperature masking agent of the masked
isocyanate is displaced to an
extent of 9/10 (mathematically
rounded-up) by a primary
monoalcohol (the primary
alcohol is generally octanol).

shelf life : in order to ensure a good
shelf life, it is preferable to
choose masked isocyanate
functions whose octanol test
shows a "release" 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-
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.

- 5 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

- 15 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 published
Byk-360 P	Byk Chemie GmbH	polyacrylate adsorbed onto silica	SM 18	June 1993
Ceraflour 961	Byk Cera	micronized polyethylene wax	XM 961	September 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
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
Reafree 4401	Resisa	saturated carboxylated polyester	107370/ 960221	February 1996
Reafree 8580	Resisa	saturated carboxylated polyester	107240/ 930309	March 1993
Reafree 8180	Resisa	saturated carboxylated polyester	8180/960521	May 1996

Definitions of abbreviations and margins of uncertainty

IPDT = PPDI (isophorone diisocyanate) trimer

HDT = HDI (hexamethylene diisocyanate) trimer

MPHB indicates that the blocking is performed with

5 methyl para-hydroxybenzoate

PHBA indicates that the blocking is performed with

para-hydroxybenzoic acid

The glosses are measured with an uncertainty of 5%

(absolute).

Example 1: 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
Ceraflour 961	20.0	20.0	20.0
Blanc Fixe 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
Appearance/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 gloss	5	6	3
60 gloss	30	35	15
85 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 gloss	5.7	6.3	2.5
60 gloss	30	35	15
85 gloss	55	70	20

** SAT = satin

Example 2: 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
Ceraflour 961	20.0	20.0
Blanc Fixe 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 gloss	3.4	2.1

60 gloss	18.7	7.0
85 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 gloss	3.4	2.2
60 gloss	18.4	7.9
85 gloss	31.1	10.4

Example 3: 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 IPDT		54.8	
N-hydroxysuccinimide masked HDT			113.0
Ceraflour 961	20.0	8.0	20.0
Blanc Fixe 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 gloss	4	19	18
60 gloss	23	50.0	55**
85 gloss	60	71	75

* yellowing

** virtually at the satin limit, see above

Example 4: structured matt black paint

MATERIALS	
SnCl ₂	3
Reafree 7000	443.0
Rhodocoat XD2D (MPHB-masked HMDT)	117.00
Dolomite	92.0
Blanc Fixe ABR	298.0
Ceraflour 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 gloss	1.2
60 gloss	6.1
85 gloss	9.5

Example 5: matt white paint

MATERIALS	
Reafree 7000	464.0
Tin oxalate	4
Rhodocoat XD2D	120.00
Titafran RL-68	290.0
Blanc Fixe ABR	90.0
Ceraflour 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 gloss	17.8
85 gloss	34.4

Example 6: colour formulations

MATERIALS	matt red paint	matt brown paint	matt black paint
Reafree 7000	454.0	453.0	451.0
Insoluble catalyst	2	2.6	3
Rhodocoat XD2D	117.0	117.0	117.0
Dolomite	92	92	92
Blanc Fixe ABR	260	264.7	290
Ceraflour 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 20 m
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 gloss	3.3	2.8	1.7
60 gloss	19.7	15.4	11.0
85 gloss	47.6	35.5	30.0

Example 7: Effect of condensation adjuvants between the masking agents and the isocyanate

STARTING MATERIALS AS % BY MASS	
Reafree 7000	450.0
Tin II oxalate	3
MPHB/PHBA (85/15) masked HDT/IPDT (85/15) comprising a variable proportion of tertiary amine	128.0
Ceraflour 961	20.0
Blanc Fixe ABR	80.0
Benzoin	3.0
TiO ₂ (RL-68)	290.0

The effect on the matt effect is collated in
5 the table below:

Firing, 200°C, 10 min on steel plate

Amount and type of tertiary amine used in the starting curing agent		Gloss at an angle of 60°
amine/NCO function ratio in % (equivalents)	as total % by mass	
(triethylamine) 3.6	1	31
(triethylamine) 0.75	0.2	42
(trioctylamine) 1	1	44
(trioctylamine) 0.2	0.2	50
(trioctylamine) 3.6	3.4	40

Example 8: Generalization to various isocyanate/masking agent couples

STARTING MATERIALS AS % BY MASS	
Reafree 7000	450.0
Tin II oxalate	3
isocyanate	120
Ceraflour 961	20.0
Blanc Fixe ABR	80.0
Benzoin	3.0
TiO ₂ (RL-68)	290.0
Amine/NCO	3% molar

The results are collated in the table below:

5

Firing, 200°C, 10 min on steel plate

Amount and type of isocyanate used		Gloss at an angle of 60°
NCO	Masking agent/agent bearing carboxylic function	
HDT	Amino caproic acid (65/35)	20
HDT	Triazole/PHBA (50/50)	17
HDT	Triazole/PHBA (70/30)	24

**CLAIMS**

1. Composition 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;

→ a polyol having the following characteristics:

· a glass transition temperature which is at least equal to about 40°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;

characterized in that it also comprises at least 1, advantageously 2 and preferably 3 of the following characteristics:

⇒ the presence of a carboxylic function,

advantageously in the form of a mixed masked isocyanate;

⇒ the presence of an advantageously solid and/or non-liposoluble esterification catalyst;

⇒ the presence of a matt-effect wax.

2. Composition according to Claim 1, characterized in that it is capable of releasing carbon dioxide under the firing conditions.



3. Composition according to either of Claims 1 and 2, characterized in that it also comprises an organic base.

4. Composition according to Claims 1 to 3, characterized in that the said organic base is an amine or a mixture of amines, which have advantageously tertiary.

5. Composition according to Claims 1 to 4, characterized in that the composition comprises

- ⇒ the presence of a carboxylic function, advantageously in the form of a masked isocyanate and bearing a carboxylic (COOH) function;
- ⇒ the presence of an esterification catalyst which is advantageously solid and/or non-liposoluble.

6. Composition according to Claims 1 to 5, characterized in that the esterification catalyst is also an allophanation catalyst.

7. Composition according to Claims 1 to 6, characterized in that the esterification catalyst is based on tin II.

8. Composition according to Claims 1 to 7, characterized in that the masked isocyanate bears the said carboxylic functions which are in the form of the reaction product of an agent bearing a carboxylic function and a function which reacts with a free isocyanate function.

9. Composition according to Claims 1 to 8, characterized in that the masked isocyanate bears the



said carboxylic functions which are in the form of the reaction product of an agent bearing a carboxylic function and a function which reacts with a free isocyanate function, and in that the said agent bearing a carboxylic function and a function which reacts with a free isocyanate function is a masking agent.

10. Composition according to Claims 1 to 9, characterized in that the ratio (in equivalents) between the carboxylic functions, on the one hand, and the isocyanate functions which are masked, free and which have reacted with any agent bearing carboxylic functions is at least equal to 5%, advantageously 10%, preferably 20%.

11. Composition according to Claims 1 to 10, characterized in that the ratio (in equivalents) between the carboxylic functions, on the one hand, and the isocyanate functions which are masked, free and which have reacted with any agent bearing carboxylic functions is at most equal to about 9/10, advantageously to about 4/5, preferably to 2/3 and more preferably one third.

12. Composition according to Claims 1 to 11, characterized in that the acid number is at most equal to 20 mg KOH/g, preferably between 3 and 15 mg KOH/g.

13. Composition according to Claims 1 to 12, characterized in that the hydroxyl number of the said polyol may range between 10 and 350 mg KOH/g, preferably between 15 and 80.



14. Composition according to Claims 1 to 13, 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).

15. Composition according to Claims 1 to 14, characterized in that the average molecular mass $\overline{Mn}$ of the binder or hydroxylated polymer of the present invention ranges between 2000 and 15,000 g/mol.

16. Composition according to Claims 1 to 15, characterized in that the said catalyst has both of the following characteristics:

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

17. Composition according to Claim 16, characterized in that it is in the form of a powder which has a d_{90} which is at most equal to about 200 micrometres, advantageously 100 micrometres.

18. Composition according to Claims 6 and 17, characterized in that the powder has a d_{10} which is at least equal to about 20 micrometres, advantageously about 50 micrometres.

19. Composition according to Claims 1 to 18, characterized in that it also contains titanium dioxide.

20. Process for preparing the compositions according to Claims 1 to 19, 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.

21. Process according to Claim 20, characterized in that the blending and extrusion temperature is at most equal to about 130°C, advantageously to about 110°C, preferably to 100°C (3 significant figures).

22. Process for preparing the compositions according to Claims 10 and 21, characterized in that the extrusion temperature is at least equal to about 60°C, advantageously to about 70°C, preferably around 80-90°C.

23. Process for preparing the compositions according to Claims 10 to 22, 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 micrometres, advantageously to 100 micrometres (2 significant figures) and a d_{10} at least equal to about 20 micrometres, advantageously to about 50 micrometres.

24. Use of the composition according to Claims 1 to 23, for coatings and in particular for paint.



25. Coating which can be obtained by the use of the composition according to Claims 1 to 9.

26. Matt or satin coating according to Claim 24, characterized in that it has waves such that it has, on average on a normal section at the surface, a height difference of from 0.2 to 5 μm .

27. Matt or satin coating according to Claims 14 and 25, characterized in that it has waves such that it has a statistical density of about 5 to 500 "waves" per millimetre.

28. Matt or satin coating according to Claims 14 to 26, characterized in that it has craters representing from 1/20 to 1/3 of the area.

29. Matt or satin coating according to Claim 27, characterized in that half of the area of the craters is due to craters whose diameter is at least equal to 1 and at most equal to 6 μm (micrometre).

PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION****International Bureau****INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)**

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(21) International application number: PCT/FR98/01681 (22) International filing date: 29 July 1998 (29.07.98) (30) Data relating to the priority: 97/09,724 30 July 1997 (30.07.97) FR 98/01,270 30 January 1998 (30.01.98) FR (71) Applicant (for all designated States except US): RHODIA CHIMIE [FR/FR]; 25, quai Paul Doumer, F-92408 Courbevoie Cedex (FR). RESISA (RESINAS SINTETICAS S.A.) [ES/ES]; Carretera Olsinelles, E-08470 Saint Celoni (ES). (72) Inventors; and (75) Inventors/Applicants (US only): BERNARD, Jean- Marie [FR/FR]; Route du Large, Saint Laurent d'Agn, F-69440 Mornant (FR). WILLIAMS, Francis, John [US/ES]; Avenida Pau Casals, 50, E-08450 Llinars del Valles (ES). VOGIN, Bernard [FR/FR]; 17, impasse de Framboisiers, F-69630 Chaponost (FR). (74) Representative: RICALES, François; Rhône-Poulenc Chimie, Direction de la Propriété Industrielle, 25, quai Paul Doumer, F-92408 Courbevoie Cedex (FR).		(81) Designated states: AL, AM, AU, AZ, BA, BB, BG, BR, BY, CA, CN, CU, CZ, EE, GE, HU, ID, IL, IS, JP, KG, KP, KR, KZ, LC, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, SL, TJ, TM, TR, TT, UA, US, UZ, VN, YU, ARIPO Patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI Patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With the International Search Report. Before expiry of the period provided for amending the claims, will be republished if such amendments are received.
As printed (54) Title: COMPOSITION USEFUL FOR OBTAINING A MATT OR DULL-GLAZED COATING, USE OF SAID COMPOSITION AND RESULTING COATING (54) Titre: COMPOSITION UTILE POUR L'OBTENTION DE REVETEMENT MAT OU SATINE, UTILISATION DE CETTE COMPOSITION ET REVETEMENT AINSI OBTENU (57) Abstract The invention concerns a composition, characterised in that it comprises by successive or simultaneous addition: an isocyanate at least partially masked having a glass transition temperature (T _g) of at least 20 °C, advantageously of at least 40 °C and a release rate at 120 °C of at most 5 %; a polyol with the following characteristics: a glass transition temperature (T _g) of at least 40 °C approximately, advantageously of at least 50 °C approximately; a hydroxyl value of at least 10 mg/g, advantageously, 15 mg/g; a mean molar mass Mn at least equal to about 1000, advantageously to 2000 g/mol. The invention is applicable to paints. (57) Abrégé La présente invention a pour objet une composition. Cette composition se définit en ce qu'elle comporte pour addition successive ou simultanée: un isocyanate au moins partiellement masqué présentant une température de transition vitreuse (parfois désignée par l'abréviation anglo-saxonne T _g) d'au moins 20 °C, avantageusement d'au moins 40 °C et un taux de libération à 120 °C d'au plus 5 %; un polyol présentant les caractéristiques suivantes: une température de transition vitreuse (parfois désignée par l'abréviation anglo-saxonne T _g) au moins égale à environ 40 °C, avantageusement au moins égale à environ 50 °C, un indice d'hydroxyle au moins égal à environ 10 mg/g, avantageusement au moins égal à environ 15 mg/g, une masse moléculaire moyenne Mn au moins égale à environ 1000, avantageusement à 2000 g/mole. Application à la peinture.		