

Description

This invention relates to thermoplastic coating compositions and in particular to such compositions in which the principal film-forming ingredients are three-component blends of acrylic polymers, cellulose acetate butyrate and monomeric plasticiser.

Thermoplastic coating compositions comprising acrylic polymers in solution in organic solvent (often referred to in the trade as "acrylic lacquers") have been known and used for many years.

A typical example for such thermoplastic coating composition is the composition described in US-A-4 168 249. This publication discloses a modern high quality coating composition which is a blend of six components, namely cellulose acetate butyrate, a polymeric plasticiser and four acrylic polymers. These acrylic polymers are respectively

- (a) polymethyl methacrylate homopolymer;
- (b) a methyl methacrylate/alkyl amino alkyl methacrylate copolymer;
- (c) a methyl methacrylate/alkyl acrylate copolymer; and
- (d) a methyl methacrylate/alkyl acrylate/ α,β -unsaturated acid copolymer which has been reacted with an alkylene imine.

Such a lacquer is an expensive product to make, both because of the cost of some of the raw materials and of the expense of manufacture. The alkyl amino alkyl methacrylates and the alkylene imines are relatively expensive materials. In addition, the alkylene imines are very dangerous materials and must be handled with extreme care; this necessitates sophisticated equipment and handling procedures for manufacture.

It is the object of the present invention to provide a thermoplastic coating composition exhibiting excellent properties which are comparable to the properties of the state-of-the-art lacquer, the components of the coating composition being carefully selected so that an uncomplicated mixture of a minimum of components is obtained and dangerous materials are avoided.

According to the present invention this object is achieved by providing a liquid coating composition comprising a mixture of

(a) a solution in volatile organic liquid of a copolymer of from 75—90% methyl methacrylate, 1.5—4.0% dimethyl aminoethyl methacrylate and 8—23.5% of monomer selected from butyl methacrylate, butyl acrylate and lauryl methacrylate, which copolymer shall have a glass transition temperature of 80°—95°C;

(b) a solution in volatile organic liquid of cellulose acetate butyrate which has a viscosity of 0.5—5.0 s when measured according to Test Method D1343 of American Society for Testing and Materials, and a hydroxyl value of 2 maximum; and

(c) a monomeric ester plasticiser compatible

with the selected mixture of the said components (a) plus (b)

such that the non-volatile constituents of (a), (b) and (c) comprise respectively 43.5—64.0%, 15.0—25.5% and 21.0—31.5% of the total weight of non-volatile material of (a) plus (b) plus (c).

We further provide a process of preparing a liquid coating composition by blending

(d) a solution in volatile liquid solvent of a copolymer of from 75—90% methyl methacrylate, 1.5—4.0% dimethyl aminoethyl methacrylate and 8—23.5% of monomer selected from butyl methacrylate, butyl acrylate and lauryl methacrylate, which copolymer shall have a glass transition temperature of 80°—95°C;

(e) a solution in volatile liquid solvent of cellulose acetate butyrate which has a viscosity of 0.5—5.0 sec when measured according to Test Method D1343 of the American Society for Testing and Materials, and a hydroxyl value of 2 maximum; and

(f) a monomeric ester plasticiser compatible with the selected mixture of the said components (d) plus (e)

such that the non-volatile constituents of (d), (e) and (f) comprise respectively 43.5—64.0%, 15.0—25.5% and 21.0—31.5% of the total weight of non-volatile material in (d) plus (e) plus (f).

The compositions of this invention provide the principal film-forming components of liquid coating compositions, which are particularly suitable for use as automotive lacquers. Paint films deposited therefrom exhibit particularly useful combinations of hardness, flexibility, gloss and in particular, adhesion to other paint substrates.

The composition of components which will confer these desirable properties is unusually narrow and to confer the optimum combination of hardness and adhesion for some uses we have found that it must be limited even further to the following preferred compatible plasticisers which are butyl benzyl phthalate or dipropylene glycol dibenzoate.

The preparation of component (a) is a conventional copolymerisation process which may be performed using standard polymerisation techniques. The glass transition temperature may be measured by using, for example a Differential Thermal Mechanical Analyser, but for the purpose of determining compliance with our invention, it is satisfactory to calculate the value from the known composition using published T_g values for homopolymers of the individual components.

As is usual with liquid coating composition, these will normally contain from 60—80% by weight of volatile solvent.

Pigments may also be incorporated in the coatings in conventional manner.

The invention is illustrated by the following examples, in which all components are expressed by weight:

Example 1

Preparation of a coating composition according to the invention and comparative testing against a commercial lacquer not according to this invention.

An acrylic copolymer solution of the following composition was prepared by conventional addition polymerisation techniques:

monomer composition	
methyl methacrylate	83 parts
n-butyl methacrylate	15 parts
dimethyl aminoethyl methacrylate	2 parts
solids	40% by weight
solvent composition	
methyl ethyl ketone	30 parts
toluene	70 parts

132.5 parts of this solution was blended with 88 parts of a 25% (by weight) solution of cellulose acetate butyrate viscosity according to ASTM D1343-69: 0.5 s) in methyl ethyl ketone and toluene (30:70 by weight) and 25.0 parts of n-butyl benzyl phthalate, to give a solution of film-forming polymer wherein the non-volatile constituents of the copolymer solution, the cellulose acetate butyrate solution and the plasticiser comprised 53%, 22% and 25% of the weight of the total non-volatile content.

The solution so-prepared was pigmented to a pigment/binder ratio of 60 with titanium dioxide pigment to produce a white lacquer.

This lacquer was tested according to the methods outlined below. A commercial acrylic refinish lacquer having the same overall general composition but in which the acrylic polymer of this example was replaced with an equal weight, based on solids content, of a methyl methacrylate homopolymer was also tested according to these methods.

Adhesion test

The lacquer was thinned with the above-mentioned solvent to a viscosity of 15—17 s in a Ford 4 viscosity cup and sprayed on to steel test panels coated with a baked, aged and lightly sanded film of commercial thermoset acrylic enamel. The film was dried in air for 24 hours and then subjected to the adhesion test of the American Society for Testing and Materials, test method D3359.

Heat distortion test

The lacquer was applied to a primed steel panel and the panel was spotted along its length with a 1% solution of egg albumen. The spots were allowed to dry overnight and the panel was then placed for 6 minutes on a thermal copper bar with a temperature gradient of from 35°C to 65°C

between its ends. The panel was washed and inspected for distortion resistance, the temperature to which each albumen spot was heated being easily determined by its position on the bar. A coating composition is considered to have acceptable distortion resistance if only those spots corresponding to temperatures above about 40°C show signs of distortion.

Recoat craze test

The lacquer was applied to a primed steel panel, allowed to air dry and aged in an oven at 65°C for 16 hours. The panel was then cooled to 25°C and a 175 µm film of the lacquer (thinned to spraying viscosity) was drawn down. The film was allowed to dry and examined for crazing (a network of fine interconnecting cracks on the surface of the dry film). The panel was returned to the oven for seven days after which it was again withdrawn, cooled to 25°C and the above-mentioned procedure repeated. The panel and the thinned lacquer used for the draw-downs were then cooled to 7°C and a third film drawn down, allowed to dry and examined for crazing.

Both lacquers performed satisfactorily in the heat distortion and recoat craze test but whereas the lacquer prepared according to the invention exhibited almost no loss of adhesion in the adhesion test, the commercial lacquer exhibited very poor adhesion.

Example 2

Use of a number of different acrylic polymers.

A number of coating compositions was prepared according to Example 1 but in each case the copolymer in that example was replaced by one of the following copolymers;

(a) methyl methacrylate (87%), n-butylmethacrylate (10%), dimethylaminoethylmethacrylate (DMAEMA) (3%).

(b) methyl methacrylate (90%), ethylacrylate (8%), DMAEMA (2%);

(c) methyl methacrylate (95%), n-butyl methacrylate (3%), DMAEMA (2%)

where (a) is according to the invention, (b) includes a monomer which is not according to the invention and (c) has proportions of comonomers which lie outside the permitted limits.

The coating compositions thus prepared were subjected to the testing procedures of Example 1. The composition (a) gave good results in all tests whereas the composition (b) performed poorly in the adhesion and heat distortion tests and the composition (c) in the adhesion and recoat craze test.

Example 3

Effect of changing the proportions of the components of the coating composition.

Example 1 was repeated but the proportions of the components were altered such that the ratio of copolymer/cellulose acetate butyrate/plasticiser was 69/6/25 instead of 53/22/25 ratio of that example. When subjected to the testing

procedures outlined in Example 1 the resultant coating composition exhibited unacceptable re-coat crazing.

Example 4

Use of various types of cellulose acetate butyrate (CAB).

Example 1 was repeated twice, in each case replacing the CAB of that example by an identical quantity of

- (a) a CAB whose hydroxyl value was 3; and
- (b) a CAB whose viscosity was 0.2 s.

When tested by the procedures outlined in Example 1, the composition containing (a) exhibited poor adhesion and that containing (b) poor re-coat crazing resistance. Prior to testing, it was also noticeable that each composition had poor gloss when compared to the composition of Example 1.

Example 5

Use of various plasticisers.

Example 1 was repeated, replacing the butyl benzyl phthalate plasticiser of that example by an identical quantity of

- (a) dipropylene glycol debenzoate
- (b) "SANTICIZER" 141 (trade mark) ex Monsanto Co. 2-ethylhexyl diphenyl phosphate
- (c) 34% coconut glycerol alkyl resin
- (d) saturated neo-pentylglycol-adipic acid polyester.

The compositions containing (a) and (b) performed satisfactorily when tested according to the procedures of Example 1 but those containing (c) and (d) exhibited poor adhesion.

Claims

1. A liquid coating composition comprising a mixture of

(a) a solution in volatile organic liquid of a copolymer of from 75—90% methyl methacrylate, 1.5—4.0% dimethyl aminoethyl methacrylate and 8—23.5% of monomer selected from butyl methacrylate, butyl acrylate and lauryl methacrylate, which copolymer shall have a glass transition temperature of 80°—95°C;

(b) a solution in volatile organic liquid of cellulose acetate butyrate which has a viscosity of 0.5—5.0 s when measured according to Test Method D1343 of the American Society for Testing and Materials, and a hydroxyl value of 2 maximum; and

(c) a monomeric ester plasticiser compatible with the selected mixture of the said components (a) plus (b)

such that the non-volatile constituents of (a), (b) and (c) comprise respectively 43.5—64.0%, 15.0—25.5% and 21.0—31.5% of the total weight of non-volatile material of (a) plus (b) plus (c).

2. A liquid coating composition according to claim 1 wherein the monomeric ester plasticiser is selected from butyl benzyl phthalate and dipropylene glycol dibenzoate.

3. A process of preparing a liquid coating composition by blending

(d) a solution in volatile liquid solvent of a copolymer of from 75—90% methyl methacrylate, 1.5—4.0% dimethyl aminoethyl methacrylate and 8—23.5% of monomer selected from butyl methacrylate, butyl acrylate and lauryl methacrylate, which copolymer shall have a glass transition temperature of 80°—95°;

(e) a solution in volatile liquid solvent of cellulose acetate butyrate which has a viscosity of 0.5—5.0 s when measured according to Test Method D1343 of the American Society for Testing and Materials, and a hydroxyl value of 2 maximum; and

(f) a monomeric ester plasticiser compatible with the selected mixture of the said components (d) plus (e)

such that the non-volatile constituents of (d), (e) and (f) comprise respectively 43.5—64.0%, 15.0—25.5% and 21.0—31.5% of the total weight of non-volatile material of (d) plus (e) plus (f).

4. A process according to claim 3 wherein the monomeric ester plasticiser is selected from butyl benzyl phthalate and dipropylene glycol dibenzoate.

Patentansprüche

1. Flüssige Anstrichzusammensetzung, die eine Mischung aus

(a) einer Lösung eines Copolymeren aus von 75—90% Methylmethacrylat, 1,5—4,0% Dimethylaminoethylmethacrylat und 8—23,5% eines Monomeren, das ausgewählt ist aus Butylmethacrylat, Butylacrylat und Laurylmethacrylat, wobei dieses Copolymere eine Glasübergangstemperatur von 80—95°C aufweisen soll, in einer flüchtigen organischen Flüssigkeit,

(b) einer Lösung von Celluloseacetatbutyrat, das eine Viskosität von 0,5—5,0 s, gemessen nach dem Testverfahren D1343 der American Society for Testing and Materials, und eine Hydroxylzahl von maximal 2 aufweist, in einer flüchtigen organischen Flüssigkeit und

(c) einem monomeren Ester-Weichmacher, der mit der gewählten Mischung der genannten Bestandteile (a) plus (b) verträglich ist,

so daß die nicht-flüchtigen Bestandteile von (a), (b) und (c) 43,5—64,0% 15,0—25,5% bzw. 21,0—31,5% des Gesamtgewichts des nicht-flüchtigen Materials aus (a) plus (b) plus (c) ausmachen, umfaßt.

2. Flüssige Anstrichzusammensetzung nach Anspruch 1, bei der der monomere Ester-Weichmacher ausgewählt ist aus Butylbenzylphthalat und Dipropylenglycoldibenzoat.

3. Verfahren zur Herstellung einer flüssigen Anstrichzusammensetzung durch Mischen

(d) einer Lösung eines Copolymeren aus von 75—90% Methylmethacrylat, 1,5—4,0% Dimethylaminoethylmethacrylat und 8—32,5% eines Monomeren, das ausgewählt ist aus Butyl-

procedures outlined in Example 1 the resultant coating composition exhibited unacceptable re-coat crazing.

Example 4

Use of various types of cellulose acetate butyrate (CAB).

Example 1 was repeated twice, in each case replacing the CAB of that example by an identical quantity of

- (a) a CAB whose hydroxyl value was 3; and
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When tested by the procedures outlined in Example 1, the composition containing (a) exhibited poor adhesion and that containing (b) poor re-coat crazing resistance. Prior to testing, it was also noticeable that each composition had poor gloss when compared to the composition of Example 1.

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- (c) 34% coconut glycerol alkyd resin
- (d) saturated neo-pentylglycol-adipic acid polyester.

The compositions containing (a) and (b) performed satisfactorily when tested according to the procedures of Example 1 but those containing (c) and (d) exhibited poor adhesion.

Claims

1. A liquid coating composition comprising a mixture of

(a) a solution in volatile organic liquid of a copolymer of from 75—90% methyl methacrylate, 1.5—4.0% dimethyl aminoethyl methacrylate and 8—23.5% of monomer selected from butyl methacrylate, butyl acrylate and lauryl methacrylate, which copolymer shall have a glass transition temperature of 80°—95°C;

(b) a solution in volatile organic liquid of cellulose acetate butyrate which has a viscosity of 0.5—5.0 s when measured according to Test Method D1343 of the American Society for Testing and Materials, and a hydroxyl value of 2 maximum; and

(c) a monomeric ester plasticiser compatible with the selected mixture of the said components (a) plus (b)

such that the non-volatile constituents of (a), (b) and (c) comprise respectively 43.5—64.0%, 15.0—25.5% and 21.0—31.5% of the total weight of non-volatile material of (a) plus (b) plus (c).

2. A liquid coating composition according to claim 1 wherein the monomeric ester plasticiser is selected from butyl benzyl phthalate and dipropylene glycol dibenzoate.

3. A process of preparing a liquid coating composition by blending

(d) a solution in volatile liquid solvent of a copolymer of from 75—90% methyl methacrylate, 1.5—4.0% dimethyl aminoethyl methacrylate and 8—23.5% of monomer selected from butyl methacrylate, butyl acrylate and lauryl methacrylate, which copolymer shall have a glass transition temperature of 80°—95°;

(e) a solution in volatile liquid solvent of cellulose acetate butyrate which has a viscosity of 0.5—5.0 s when measured according to Test Method D1343 of the American Society for Testing and Materials, and a hydroxyl value of 2 maximum; and

(f) a monomeric ester plasticiser compatible with the selected mixture of the said components (d) plus (e)

such that the non-volatile constituents of (d), (e) and (f) comprise respectively 43.5—64.0%, 15.0—25.5% and 21.0—31.5% of the total weight of non-volatile material of (d) plus (e) plus (f).

4. A process according to claim 3 wherein the monomeric ester plasticiser is selected from butyl benzyl phthalate and dipropylene glycol dibenzoate.

Patentansprüche

1. Flüssige Anstrichzusammensetzung, die eine Mischung aus

(a) einer Lösung eines Copolymeren aus von 75—90% Methylmethacrylat, 1,5—4,0% Dimethylaminoethylmethacrylat und 8—23,5% eines Monomeren, das ausgewählt ist aus Butylmethacrylat, Butylacrylat und Laurylmethacrylat, wobei dieses Copolymere eine Glasübergangstemperatur von 80—95°C aufweisen soll, in einer flüchtigen organischen Flüssigkeit,

(b) einer Lösung von Celluloseacetatbutyrat, das eine Viskosität von 0,5—5,0 s, gemessen nach dem Testverfahren D1343 der American Society for Testing and Materials, und eine Hydroxylzahl von maximal 2 aufweist, in einer flüchtigen organischen Flüssigkeit und

(c) einem monomeren Ester-Weichmacher, der mit der gewählten Mischung der genannten Bestandteile (a) plus (b) verträglich ist,

so daß die nicht-flüchtigen Bestandteile von (a), (b) und (c) 43,5—64,0% 15,0—25,5% bzw. 21,0—31,5% des Gesamtgewichts des nicht-flüchtigen Materials aus (a) plus (b) plus (c) ausmachen, umfaßt.

2. Flüssige Anstrichzusammensetzung nach Anspruch 1, bei der der monomere Ester-Weichmacher ausgewählt ist aus Butylbenzylphthalat und Dipropylenglycoldibenzoat.

3. Verfahren zur Herstellung einer flüssigen Anstrichzusammensetzung durch Mischen

(d) einer Lösung eines Copolymeren aus von 75—90% Methylmethacrylat, 1,5—4,0% Dimethylaminoethylmethacrylat und 8—32,5% eines Monomeren, das ausgewählt ist aus Butyl-



methacrylat, Butylacrylat und Laurylmethacrylat, wobei dieses Copolymere eine Glasübergangstemperatur von 80—95°C aufweisen soll, in einem flüchtigen flüssigen Lösungsmittel,

(e) einer Lösung von Celluloseacetatbutyrat, das eine Viskosität von 0,5—5,0 s, gemessen nach dem Testverfahren D1343 der American Society for Testing and Materials, und eine Hydroxylzahl von maximal 2 aufweist, in einem flüchtigen flüssigen Lösungsmittel und

(f) eines monomeren Ester-Weichmachers, der mit der gewählten Mischung der genannten Bestandteile (d) plus (e) verträglich ist,

so daß die nicht-flüchtigen Bestandteile von (d), (e) und (f) 43,5—64,0%, 15,0—25,5% bzw. 21,0—31,5% des Gesamtgewichts der nicht-flüchtigen Materialien aus (d) plus (e) plus (f) ausmachen.

4. Verfahren nach Anspruch 3, bei dem der monomere Esterweichmacher ausgewählt ist aus Butylbenzylphthalat und Dipropylenglycol-dibenzoat.

Revendications

1. Composition liquide de revêtement, comprenant un mélange

(a) d'une solution dans un liquide organique volatil d'un copolymère de 75 à 90% de méthacrylate de méthyle, 1,5 à 4,0% de méthacrylate de diméthylaminoéthyle et 8 à 23,5% d'un monomère choisi entre le méthacrylate de butyle, l'acrylate de butyle et le méthacrylate de lauryle, ce copolymère devant avoir une température de transition vitreuse de 80 à 95°C;

(b) d'une solution dans un liquide organique volatil d'acéto-butyrat de cellulose qui a une viscosité de 0,5 à 5,0, mesurée conformément à la méthode d'essai D1343 de l'American Society for Testing and Materials, et un indice d'hydroxyle égal à 2 au maximum; et

(c) d'un plastifiant qui est un ester monomérique compatible avec le mélange choisi desdits composants (a) plus (b),

de manière que les constituants non volatils de (a), (b) et (c) constituent, respectivement, 43,5—64,0%, 15,0—25,5% et 21,0—31,5% du poids total de la matière non volatile de (a) plus (b) plus (c).

2. Composition liquide de revêtement suivant la revendication 1, dans laquelle l'ester monomérique plastifiant est choisi entre le phtalate de butyl-benzyle et le dibenzoate de dipropylène-glycol.

3. Procédé de préparation d'une composition liquide de revêtement par mélange

(d) d'une solution dans un solvant liquide volatil d'un copolymère de 75 à 90% de méthacrylate de méthyle, 1,5 à 4,0% de méthacrylate de diméthylaminoéthyle et 8 à 23,5% d'un monomère choisi entre le méthacrylate de butyle, l'acrylate de butyle et le méthacrylate de lauryle, ce copolymère devant avoir une température de transition vitreuse de 80—95°;

(e) d'une solution dans un solvant liquide volatil d'acéto-butyrat de cellulose qui a une viscosité de 0,5 à 5,0 mesurée conformément à la méthode d'essai D1343 de l'American Society for Testing and Materials et un indice d'hydroxyle au maximum égal à 2; et

(f) d'un plastifiant qui est un ester monomérique compatible avec le mélange choisi desdits composants (d) plus (e)

de manière que les constituants non volatils de (d), (e) et (f) constituent, respectivement, 43,5—64,0%, 15,0—25,5% et 21,0—31,5% du poids total de matière non volatile de (d) plus (e) plus (f).

4. Procédé suivant la revendication 3, dans lequel l'ester monomérique plastifiant est choisi entre le phtalate de butyl-benzyle et le dibenzoate de dipropylène-glycol.

