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(54) Titre : ADHESIF POUR MATIERES PLASTIQUES DE TYPE METHACRYLATE
(54) Title: ADHESIVE FOR METHACRYLATE PLASTICS

(57) Abrégé/Abstract:
Methacrylic plastics are bonded to each other and other plastics by applying an adhesive of a low molecular weight alkyl formate or a volatile adhesive mixture or adhesive varnish containing a low molecular weight alkyl formate to at least one bonding surface of plastics to be bonded to each other, at least one of the plastics being a methacrylate plastic, and bonding plastic surfaces to each other.

ABSTRACT OF THE DISCLOSURE

Methacrylic plastics are bonded to each other and other plastics by applying an adhesive of a low molecular weight alkyl formate or a volatile adhesive mixture or adhesive varnish containing a low molecular weight alkyl formate to at least one bonding surface of plastics to be bonded to each other, at least one of the plastics being a methacrylate plastic, and bonding plastic surfaces to each other.

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TITLE OF THE INVENTION

ADHESIVE FOR METHACRYLATE PLASTICS

BACKGROUND OF THE INVENTION

Field of the Invention:

The present invention relates to adhesives for methacrylate plastics in the form of volatile organic fluids or in the form of adhesive varnishes consisting of a solution of a polymer in such a fluid.

Description of the Background

EP-B 867 application describes an adhesive for methacrylate plastics which contains nitromethane or nitroethane as a solvent. Optimum adhesive properties are found when mixtures of nitromethane and dichloromethane are employed.

Task and Solution

Dichloromethane and other chlorinated hydrocarbons are considered toxic and carcinogenic. For this reason, there is a need for an adhesive for methacrylate plastics that does not contain chlorinated hydrocarbons, but has properties comparable to those of nitromethane-dichloromethane mixtures. Requirements include short superficial dissolving times and low stress corrosion cracking, as well as low toxicity.

SUMMARY OF THE INVENTION

Accordingly, one object of the present invention is to provide an adhesive material for methacrylate plastics which achieves bonding of such plastics of improved strength, which

adhesive does not contain a chlorinated hydrocarbon component.

Briefly, this object and other objects of the present invention as hereinafter will become more readily apparent can be attained in a method of bonding methacrylate plastic to each other and other plastic materials by applying adhesive of a low molecular weight alkyl formate or a volatile adhesive mixture or adhesive varnish containing a low molecular weight alkyl formate to at least one bonding surface of plastics to be bonded to each other, at least one of said plastics being a methacrylate plastic, and bonding the plastic surfaces to each other.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is directed to a low-molecular weight alkyl formate as an adhesive or as an additive to volatile adhesive mixtures, or as an additive to adhesive varnishes for bonding parts of methacrylate plastics to each other or with other plastics. A preferred aspect of the invention is the use of a mixture of at least 15 wt.% of a low-molecular weight alkyl formate and up to 85 wt. % of other volatile organic fluids free of chlorinated hydrocarbons and having a boiling point not exceeding 200°C, particularly nitromethane and/or nitroethane.

During the superficial dissolving process, the swelling plastic surface exerts a significant swelling pressure on the material layer beneath it, possibly resulting in tearing. The adhesive of the present invention has the surprising effect that swelling, softening and dissolving processes interact in

such a way that tearing is largely suppressed, and tears that do form are largely closed again due to the effect of the adhesive. Although not all of the advantageous properties of the known nitromethane-dichloromethane mixtures are obtained, the adhesives according to the invention, because of their complete absence of chlorinated hydrocarbons and an improved strength of the adhesive bonds, represent an important improvement in the field of methacrylate plastics bonding.

Volatile Adhesives

A volatile adhesive of the present invention is one which superficially dissolves plastic surfaces and brings about adhesion, while the adhesive completely evaporates again. These solvents are suitable for bonding parts with an exact fit relative to each other. It is advantageous that they have boiling points from 30 to 150°C (under normal pressure). Suitable volatile solvents include alkyl formates such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-amyl, isoamyl, and n-hexyl formates. Because of their high volatility, methyl formate and ethyl formate are particularly preferred.

Mixtures of at least 15 wt. % of a low-molecular alkyl formate and up to 85 wt. % of other volatile organic fluids free of chlorinated hydrocarbons having a boiling point not exceeding 200°C have various advantages compared to the alkyl formates by themselves. While methyl and ethyl formate alone may result in tearing, particularly when bonding plastic parts with internal tensions, this risk is much lower when using

mixtures with nitromethane and nitroethane. Mixtures of 25 to 75 wt. % methyl formate and/or ethyl formate and 75 to 25 wt. % nitromethane and/or nitroethane are preferred. The addition of other solvents, such as ketones or esters, e.g. ethyl acetate, are also within the scope of the invention.

By adding 0.5 to 10 wt.% of alcohols having boiling points between 70 and 280°C, improvements in the quality of the adhesive joints can be achieved. Because of lower volatility, they are temporarily concentrated during the drying of the adhesion joint at their surface. This prevents flaws in the surface that may result from premature skin formation or from condensation of water from humid ambient air because of cooling caused by evaporation. An addition of n-butanol, e.g. prevents wrinkling; the addition of phenoxyethanol prevents the clouding of the adhesive joint in the case of high air humidity.

Adhesive Varnishes

Adhesive varnishes are adhesives with a polymer content which remains in the adhesive joint after the evaporation of the volatile components and produces the bond between the bonded parts. Adhesive varnishes are advantageous if the parts to be bonded cannot be form-fitted together, and if during the bonding, distances of e.g. 0. 1 to 1 mm must be bridged.

Like any adhesive resin, the dissolved polymer must have a sufficient adhesiveness to the material of the parts to be bonded, and also a sufficient internal strength. These

conditions are best fulfilled if the dissolved polymer itself is a methacrylate plastic, e.g., polymethylmethacrylate. Thermoplastic polymers are preferred. Other suitable adhesive resins are polyvinyl acetate, polyvinyl ether, or cellulose acetobutyrate. The polymer content has an upward limit based on the viscosity of the solution. The solution viscosity at 20°C generally should not exceed 10,000 mPa s. It is advantageous to use approximately 3 to 30 wt. % of a polymer which results in a viscosity of the solution ranging from 500 to 2,000 mPa s.

Bonding of Methacrylate Plastics

The adhesives to be used according to the invention primarily serve to bond parts of methacrylate plastics with each other or with parts of other plastics such as polyvinyl chloride, polystyrene, butadiene-styrene plastics, ABS plastics, or cellulose esters (CAB). In order to bond methacrylate plastics to other materials such as wood, paper, cardboard, leather, metal, ceramic material, glass, porcelain, the adhesive varnishes of the invention are preferably used.

A suitable methacrylate plastic is in particular acrylic glass. Examples are poured, extruded, or injection-molded polymethylmethacrylate or copolymers of the methylmethacrylate with no more than 10 wt. % of other ethylene-unsaturated radically polymerizable monomers, particularly low-molecular alkyl acrylates. The methacrylate plastics also include methylmethacrylate-acrylonitrile copolymers, methylmethacrylate-styrene-maleic anhydride copolymers,

shock-resistant modified polymethylmethacrylate, and the like.

To bond with volatile adhesives, the closely fitting bonding surfaces are wetted with the adhesive and joined in the desired position. The adhesive also can be applied to the edge of the contact surface, so that it is drawn by itself into the gap between the bonding parts because of capillary force. When using adhesive varnishes, it is sufficient if one of the plastic surfaces to be bonded is coated with a thickness sufficient to fill the joint, and to join the parts together.

The superficial dissolving time, during which the parts to be bonded are easily moved relative to each other, usually lasts approximately 30 to 90 seconds. After this, a sufficient stability is achieved for holding the parts to be bonded in the desired position even without support. The adhesive joint is then left to stabilize, preferably under a slight pressure, because of evaporation of the volatile adhesive components. After a drying time of 1 to 4 hours, a high adhesion strength is obtained. It clearly increases during the course of 1 to 2 weeks, or preferably by tempering for 2 to 6 hours at 60 to 90°C.

Having generally described this invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.

Determination of Adhesive Strength

The following table contains combined tension and shear

resistance values measured on bonded parts of extruded and poured acrylic glass with the following adhesives of the invention:

A) Volatile adhesive (wt. %), viscosity 500-700 mPa s: 44% ethyl formate, 44% nitroethane, 4 % phenoxyethanol, 3 % n-butanol, 5 % acetic ester;

B) Adhesive varnish (wt.%), viscosity 750- 1,000 mPa s: 39 % ethyl formate, 39 % nitroethane, 4 % phenoxyethanol, 3 % n-butanol, 5 % acetic ester, 10% polymethylmethacrylate.

These examples of the invention are compared with known adhesives C and D with the compositions:

C) Volatile adhesive (wt. %): 52 % dichloromethane, 40 % nitromethane, 5 % phenoxyethanol, 3% ethanol

D) Adhesive varnish (wt.%): 44 % dichloromethane, 36 % nitromethane, 7 % phenoxyethanol, 3% ethanol, 10% polymethylmethacrylate.

The combined tension and shear resistance is measured by subjecting a 2 cm^2 large adhesive area to tensile stress in the direction of the adhesive area. The first measurement is taken after drying at room temperature for 5 days, the second measurement after tempering over 5 hours at 80°C.

Bonded plastics -adhesive		Comb. tension and shear resistance in mPa after 5 days	after tempering
Cast ~~Poured~~ acrylic glass (PLEXIGLAS GS)			Nov. 24, 94
- volatile adhesive	A	31.3	42.3
- adhesive varnish	B	31.0	46.0
- volatile adhesive	C	30.3	33.9
- adhesive varnish	D	27.6	31.7
Extruded acrylic glass (PLEXIGLAS XT)			
- volatile adhesive	A	39.3	51.6
- adhesive varnish	B	40.1	54.2
- volatile adhesive	C	37.9	43.2
- adhesive varnish	D	34.9	43.6

Nov. 24, 94

Bonding Under Bending Stress

Two strips measuring 85 x 10 x 2 mm of extruded acrylic glass were placed on top of each other with their surfaces and connected at the ends with lead adhesive tape. The strips were then elastically spread apart by way of spacers placed between them in the center, resulting in a uniform bending radius of 500-600 mm, corresponding to a bending stress of 6 Mpa. The strips subject to bending stress were glued with their edges onto a plane plate of extruded acrylic glass. After drying, the tearing and bubbling in the adhesive area and on the convex outside surfaces were evaluated.

For bonding, the volatile adhesive A and the adhesive varnish B according to the invention, and for control purposes the liquid adhesive C and adhesive varnish D based on dichloromethane/nitromethane were used. Findings:

A: no tears in bonded area,
many fine tears along edge, few bubbles
B: no tears in bonded area,
many fine tears in outer bonding edge,
C: no tears in bonded area,
very fine tears, in part closed by dissolving, on edge
D: no tears, many bubbles.

Having now fully described the invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit or scope of the invention as set forth herein.

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

1. A method of bonding methacrylate plastics to each other and other plastic materials, comprising:

applying an adhesive of a low molecular weight alkyl formate or a volatile adhesive mixture or adhesive varnish containing a low molecular weight alkyl formate to at least one bonding surface of plastics to be bonded to each other, at least one of said plastics being a methacrylate plastic; and

bonding the plastic surfaces to each other.

2. The method of Claim 1, wherein said adhesive is or contains a mixture of at least 15 wt% of a low molecular weight alkyl formate and up to 85 wt % of other volatile organic fluids free of chlorinated hydrocarbons and having a boiling point not exceeding 200°C.

3. The method of Claim 2, wherein said alkyl formate is methyl formate, ethyl formate or combinations thereof.

4. The method of Claim 2 or 3, wherein said other volatile organic fluid is nitromethane, nitroethane or combinations thereof.

5. The method of Claim 2 or 3, wherein said adhesive mixture or varnish contains 0.5 to 10 wt% of an alcohol having a boiling point between 70° and 280°C.

6. The method of Claim 2, wherein the adhesive material contains dissolved polymer and has a solution viscosity which does not exceed 10,000 mPa s at 20°C.

7. The method of Claim 1, wherein a plastic being bonded is acrylic glass.

8. The method of Claim 7, wherein said acrylic glass is extruded acrylic glass.