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(54) Title: ADHESION PROMOTERS FOR PLASTISOLS

(57) Abstract: The invention relates to adhesion promoters for plastisols, characterized in that the adhesion promoter comprises not only a polyaminoamide but also propylene glycol monophenyl ether (phenoxypropanol), to a process for the production of coatings and adhesive bonds for materials, and also to plastisols in which these adhesion promoters are used concomitantly.

Adhesion promoters for plastisols

The invention relates to adhesion promoters based on polyaminoamides, comprising propylene glycol monophenyl ether, and also to the use of these adhesion promoters for improving adhesion of PVC plastisols.

Plastisols are widely used for protecting metallic surfaces from corrosion. In particular in the automotive sector, plastisols are used for the waterproofing, bonding and sealing of seams and joints, and for protecting external surfaces, such as underbodies and sills.

These applications mostly use plastisols based on PVC polymers or on PVC copolymers. These plastisols are composed of fine polymer particles which have been dispersed in a non-volatile plasticizer. At room temperature, the polymer particles are insoluble in the liquid phase. At a higher temperature (gelling temperature), the polymer particles dissolve in the plasticizer. On cooling, the homogeneous solution hardens to give a flexible or rigid coating. The main methods used to apply these coatings to the materials to be protected are brushing, rolling or spraying.

The formulation of plasticized polyvinyl chloride coating compositions (plastisols), and their preparation and use is extensively described in: Krekeler / Wick, Kunststoff-Handbuch [Plastics Handbook] (1963), Volume II, Part 1, pp. 396 ff.

A significant criterion for the quality of plastisols applied in this way is their adhesion to the coated material. Relatively low adhesion of the protective layer increases the risk of penetration of aggressive fluids. For example, water can migrate under the coating and corrode the metal. This becomes increasingly possible as the adhesion of the protective film to the metal becomes lower. To increase the adhesion of these coatings, therefore, industry adds adhesion-improving additives to the plasticized polyvinyl chloride. The function of the adhesion promoters is to bring about lasting adhesion to the surfaces of commonly encountered materials, such as non-degreased untreated steel, galvanised metal sheet or tin-coated metal sheet, electrocoated metal sheet, etc.

There are previously-developed adhesion promoters for PVC plastisols. Examples of these adhesion promoters are polyamines, epoxy resins, capped isocyanates, organofunctional silanes, and esters of acrylic or methacrylic acid.

In most cases, the adhesion promoters used comprise polyaminoamides containing imidazoline groups. These give good adhesion to the substrate, even if the concentrations in the plastisol are relatively small. These polyaminoamides are prepared from what are known as polymerized fatty acids and an excess of polyethylene polyamines, by polycondensation. The expression polymerized fatty acids encompasses polymerized fatty acids prepared from unsaturated, naturally occurring or synthetic, monobasic, aliphatic acids having from 12 to 22 carbon atoms, preferably 18 carbon atoms. The fatty acids may be polymerized by a well-known process (for example as in DE 25 06 211 A1). These adhesion promoters are described by way of example in DE 26 54 871 A1 and in DE 32 01 265 A1. DE 44 00 509 A1 describes plastisol compositions in which the addition of secondary adhesion promoters in the form of trihydric or higher-functionality aliphatic alcohols and/or alkanolamines, in addition to the conventional adhesion promoters based on polyaminoamides, to PVC plastisols improves their adhesion properties, in particular on sheets coated by a cataphoretic process. In the experimental section of that specification, glycerol is used as secondary adhesion promoter. However, these secondary adhesion promoters have to be added in addition to the primary polyaminoamide adhesion promoters, the amount of which incorporated into the plastisol is usually about 1% by weight (based on the total amount of plastisol). The viscosity of the polyaminoamides used is moreover generally very high, and incorporation into the plastisol is therefore rendered difficult.

In order to lower the viscosity and thus provide good processability of the adhesion promoter, e.g. for the mixing of the adhesion promoter into the plastisol, and also to lower the price of these adhesion promoters, the adhesion promoters, which are generally of very high viscosity, are often formulated with plasticizers. However, plasticizers have an adverse effect on the adhesion of the PVC plastisol to the substrate in most cases. Plasticizers often used are phthalic esters, e.g. dibutyl phthalate, dioctyl phthalate or dinonyl phthalate. One adverse effect which has been observed is their low effectiveness in diluting the adhesion promoter. Relatively high amounts of these phthalates have to be used if sufficient processability is to be provided.

However, larger amounts of these plasticizers have an adverse effect on adhesion to the substrate. In addition, dialkyl phthalates used as plasticizers in adhesion promoters bring about a rise in viscosity of the adhesion promoter over the course of time, this being explicable via cleavage of the ester and reaction with the free amine groups in the polyaminoamide/imidazoline. The usefulness of these adhesion promoters is therefore subject to a time limit, because after some time incompatibility arises, and finally gelling occurs. In addition, the toxicological risks posed by the dialkyl phthalates class of product have recently caused their use to be criticized. DE 694 02 959 T2 claims a process for the preparation of specific polyamide resins which, according to Claim 9, comprise dioctyl phthalate, benzyl alcohol, and diisopropyl naphthalene as plasticizers. EP 0 658 574 A1 describes the use of amidoamines, imidoamines and ester amines based on a) copolymers of monounsaturated carboxylic acids and ethylenically unsaturated compounds and b) polyamines as adhesion promoters, likewise using the abovementioned compounds as plasticizers. However, as the proportion in the adhesion promoter rises, the use of these plasticizers again leads to impairment of adhesion of the plastisol to the substrate.

It is therefore an object of the invention to provide an additive which is intended for adhesion promoters in PVC plastisols and which is compatible with the polyaminoamide, has good effectiveness in diluting the adhesion promoter, and is stable with respect to viscosity, and, finally, has minimum effect on the adhesion of the PVC plastisols to the substrate.

According to the invention, this object is achieved by using adhesion promoters which comprise not only a polyaminoamide but also propylene glycol monophenyl ether (phenoxypropanol). Depending on the adhesion behaviour and on the amount of the respective polyaminoamide used, the amount of phenoxypropanol advantageously used may vary within a very wide range. However, on the basis of the commonly used proportions of adhesion promoter, from 0.5 to 2% by weight in the respective plastisol composition, the amount of phenoxypropanol used, based in each case on the total amount of the adhesion promoter, should advantageously be at least 10% by weight and at most 60% by weight, preferably from 25 to 55% by weight, particularly preferably from 40 to 50% by weight. Surprisingly, these compounds (phenoxypropanol) have no adverse effect on the adhesion of the PVC plastisol to the substrate, even in these very large amounts of from 40 to 50% by weight in the adhesion promoter. It would have been expected that the adhesion of the PVC plastisols to the substrate would fall off as the amount of additive in the adhesion promoter rises, because the proportion of the adhesion promoter itself becomes smaller. However,

even when the proportion of phenoxypropanol in the adhesion promoter is 50%, there is no, or at least hardly any, effect on the adhesion of the PVC plastisol to the substrate. The viscosity of the adhesion promoters is low, and the adhesion promoter is stable in terms of viscosity.

This invention therefore provides adhesion promoters for PVC plastisols, characterized in that they comprise not only a polyaminoamide but also phenoxypropanol, the amount of phenoxypropanol present in the adhesion promoter, based on the total amount of adhesion promoter, being at least 10% by weight and at most 60% by weight, preferably from 25 to 55% by weight, particularly preferably from 40 to 50% by weight.

The invention also provides a process for the production of coatings and adhesive bonds for materials by applying plastisols based on fine-particle polyvinyl chloride or, respectively, vinyl chloride copolymers, which comprise conventional fillers, additives, plasticizers and adhesion promoters, characterized in that use is made of adhesion promoters which comprise not only a polyaminoamide but also phenoxypropanol in amounts, based on the total amount of adhesion promoter, of at least 10% by weight and at most 60% by weight, preferably from 25 to 55% by weight, particularly preferably from 40 to 50% by weight.

The adhesion promoters are added in proportions of from 0.3 to 5% by weight, preferably from 0.5 to 2% by weight, particularly preferably 1% by weight, based on the weight of the plastisol, and the mixture is homogenized, and the plastisols thus prepared are stoved on the material at temperatures of 90°C or above, preferably at from 120°C to 160°C.

The invention also provides plastisols for the production of coatings on materials, comprising fine-particle polyvinyl chloride or, respectively, vinyl chloride copolymers, conventional plasticizers, fillers, additives and adhesion promoters, characterized in that an adhesion promoter of the invention is present.

Examples

In examples 2 to 5 below, the polyaminoamide adhesion promoter Euretek 563 from example 1 is heated with stirring to about 100°C and the appropriate additives are added, and the mixture is then homogenized.

Example 1 (comparative example):

Euretek[®] 563 (commercial adhesion promoter based on a polyaminoamide from the company Vantico AG).

Example 2 (comparative example):

60% Euretek 563; 40% of dioctyl phthalate.

Example 3 :

60% Euretek 563; 40% of phenoxypropanol.

Example 4:

50% Euretek 563; 50% of phenoxypropanol.

Example 5 (comparative example):

80% Euretek 563; 20% of glycerol.

Preparation of plastisols:

1% of the abovementioned polyaminoamide of examples 1 to 5, based on the entire mixture, is added as adhesion promoter to a plastisol composed of:

35% of diisononyl phthalate; 25% of paste PVC (e.g. Solvic[®] 347 MB); 16.0% of coated chalk (Socal[®] 312); 16.5% of naturally occurring chalk (Juraperle); 2.0% of CaO; 0.2% of ZnO and 4.3% of Exxsol[®] 80.

Of course, the adhesion promoters may also be added to conventional plastisol formulations other than those given above in order to obtain the self-adhesive plastisols of the invention.

The adhesion achievable using the plastisols of the invention is determined manually. For this, use is made of Cathoguard 400 CEC sheets from the company BASF. Dimensions of adherends 25 x 100 mm.

Method:

A spatula is used to apply a strip of the PVC plastisol, about 1.5 cm in width and about 5 cm in length, to the CEC strip, and a doctor is used to spread the plastisol to give a test strip of width 1.5 cm with a thickness of 1.5 mm. The test specimen is placed in the temperature-controlled drying cabinet and stoved at 140°C for 30 minutes. After stoving, the test specimen is removed from the drying cabinet. After cooling (for at least 2 hours), the adhesion test can be carried out. For this, a knife is used to make an incision to a width of about 0.5 cm in both sides of the test strip. The test strip is then tested manually for peelability.

The following classification system is used for assessment:

—	No adhesion at all
O	Strip can easily be peeled; slight film of plastisol remaining on the CEC layer
⊕	Strip difficult to peel; slight film of plastisol remaining on the CEC layer
+	Strip difficult to peel and breaks on peeling; significant film of plastisol remaining on the CEC layer
++	Strip cannot be peeled

The results of the measurements are listed in table 1 below.

Table 1:

Example	Viscosity at 25°C [mPa•s]	Viscosity at 75°C [mPa•s]	Manual Adhesion	Viscosity at 75°C [mPa•s] after storage 30 days/50°C	Appearance after storage 30 days/50°C
1	n.m ^{*)}	16500	++	16600	clear
2	22300	1300	+	6000	cloudy/ incompatible
3	16200	810	++	815	clear
4	11900	500	++	505	clear
5	n.m ^{*)}	12000	⊕	12600	clear

^{*)} not measurable at 25°C (viscosity too high)

The viscosities were measured using a VT 550 Haake rotary viscosimeter in accordance with the manufacturer's instructions.

Interpretation of results:

As can be seen from the table, the adhesion promoters of the invention (examples 3 and 4) have low viscosity and are therefore easier to process. In contrast with comparative example 2, the adhesion promoters of the invention are storage-stable, even after storage at relatively high temperatures, and therefore remain available for use by the user even after a prolonged storage time. Surprisingly, use of the inventive adhesion promoters with 40% (example 3) and even 50% (example 4) content of phenoxypropanol, based on the total amount, gives excellent adhesion of the plastisols to the substrate. Use of the adhesion promoter from comparative examples 2, and in particular 5, gives adhesion which can sometimes carry marked reduction as dilution increases. The adhesion of the plastisols to the substrates would also have been expected to fall when phenoxypropanol is used in the adhesion promoter, as the proportion of phenoxypropanol rises. Surprisingly, even with 50% of phenoxypropanol in the adhesion promoter the adhesion is not reduced and remains good. This result was not foreseeable.

Patent Claims

- 1) Adhesion promoter for plastisols, characterized in that the adhesion promoter comprises not only a polyaminoamide but also propylene glycol monophenyl ether (phenoxypropanol).
- 2) Adhesion promoter according to Claim 1, characterized in that the proportion of phenoxypropanol is at least 10% by weight and at most 60% by weight, based on the total amount of adhesion promoter.
- 3) Adhesion promoter according to Claim 2, characterized in that the proportion of phenoxypropanol is from 25 to 55% by weight, preferably from 40 to 50% by weight, based on the total amount of adhesion promoter.
- 4) Process for producing coatings and adhesive bonds for materials, by applying the plastisols based on fine-particle polyvinyl chloride or, respectively, vinyl chloride copolymers, which comprise conventional fillers, additives, plasticizers and adhesion promoters, characterized in that use is made of an adhesion promoter according to any of Claims 1 to 3.
- 5) Process according to Claim 4, characterized in that the adhesion promoter is added in proportions of from 0.3 to 5% by weight, based on the weight of plastisol, and the mixture is homogenized, and the plastisols thus prepared are stoved on the material at temperatures greater than or equal to 90°C, preferably from 120°C to 160°C.
- 6) Process according to Claim 5, characterized in that the adhesion promoter is added in proportions of from 0.5 to 2% by weight, preferably 1% by weight, based on the weight of the plastisol.
- 7) Plastisols for the production of coatings on materials, comprising fine-particle polyvinyl chloride or, respectively, vinyl chloride copolymers, conventional plasticizers, fillers, additives and adhesion promoters, characterized in that an adhesion promoter according to any of claims 1 to 3 is present.

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D5/00 C09J5/02 C09D127/06 C08K5/06 C08K5/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D C09J C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 26 54 871 A (SCHERING AG) 8 June 1978 (1978-06-08) cited in the application ---	
A	WO 95 19387 A (HENKEL KGAA ;KARRER RANDOLF (DE); COLLET MICHEL (FR); ABEL JEAN CL) 20 July 1995 (1995-07-20) & DE 44 00 509 A (HENKEL) 13 July 1995 (1995-07-13) cited in the application ---	
A	WO 01 94464 A (HENKEL CORP ;HABJANIC FELIKS (US); HUBERT JAMES (US)) 13 December 2001 (2001-12-13) ---	
A	EP 0 171 850 A (CHEM PLAST SPA) 19 February 1986 (1986-02-19) -----	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 2654871	A	08-06-1978	DE 2654871 A1	08-06-1978
			BE 861449 A1	02-06-1978
			DK 493877 A	04-06-1978
			FR 2372862 A1	30-06-1978
			GB 1577583 A	29-10-1980
			IE 46099 B1	23-02-1983
			IT 1089313 B	18-06-1985
			LU 78615 A1	20-04-1978
			NL 7710812 A ,B,	06-06-1978
			PL 202572 A1	28-08-1978
			SE 439319 B	10-06-1985
			SE 7713634 A	04-06-1978
			US 4146520 A	27-03-1979

WO 9519387	A	20-07-1995	DE 4400509 A1	13-07-1995
			WO 9519387 A1	20-07-1995
			EP 0739375 A1	30-10-1996
			TR 28973 A	05-08-1997
			ZA 9500179 A	12-07-1995

WO 0194464	A	13-12-2001	AU 6323201 A	17-12-2001
			CA 2413972 A1	13-12-2001
			EP 1301568 A1	16-04-2003
			WO 0194464 A1	13-12-2001

EP 0171850	A	19-02-1986	IT 1180214 B	23-09-1987
			AT 68007 T	15-10-1991
			DE 3584277 D1	07-11-1991
			EP 0171850 A1	19-02-1986
			ES 8802431 A1	16-09-1988
			JP 2025678 C	26-02-1996
			JP 6021265 B	23-03-1994
			JP 61053347 A	17-03-1986
			US 4717746 A	05-01-1988
