

This invention relates to an improved adhesive for mouldings of rigid PVC and more especially to a material which, despite a significantly reduced tendency towards stress-induced corrosion, even in critical applications, still satisfies current requirements in regard to storage life, conformity with standards, creep strength and gap-filling ability.

For bonding mouldings of rigid PVC, for example corresponding PVC pressure pipes, it is common practice to use adhesive compositions which contain powder-form PVC dissolved in a suitable PVC solvent or solvent system. Characteristic application properties of adhesive systems such as these, such as pot life and swelling behaviour, may be regulated as required through the choice of the solvent mixtures.

The bonding principle is based on the swelling, dissolving and diffusing power of the solvents. The solvents diffuse into the underlying material, causing it to swell, and, in conjunction with the PVC introduced in solution, establish the bond when the adherend and substrate are pressed together. The solvents desorb over a period of time which cannot be exactly defined, so that a homogeneous bond is obtained.

Systematic investigations have shown that, on account of their dissolving, evaporating and plasticizing properties, the solvents present in adhesives of the type in question have a different effect on possible structural damage arising out of the bonds. This becomes particularly critical when, in the case of heavily stressed mouldings, for example 4-way fittings, the mechanical load applied in any event is accompanied by additional accumulations of adhesive through displacement of the excess adhesive applied to the inside of the sleeve into the sleeve core.

The teaching according to the invention which provides improved adhesive compositions for rigid PVC is based inter

alia on the observation that certain solvent components known per se as good PVC-solvents are responsible for the unwanted structural damage mentioned above. Tests conducted by Applicants have shown that cyclic PVC-solvents, namely cyclohexanone, and - to a certain extent - tetrahydrofuran can cause damage, more particularly stress-induced corrosion. Both tetrahydrofuran and cyclohexanone are known per se as good PVC-solvents, cf. for example "Kunststoffe 70", (1980), 313 to 318. Their use in adhesive compositions of the type in question here is basically advantageous or even necessary in the light of the various requirements which the adhesive compositions or rather the rigid PVC bonds ultimately formed have to satisfy.

Thus, the adhesives in question have to comply with various standard requirements in regard to their creep strength, including DIN 16 970, KIWA No. 55, BSI 4346, ASTM 2564 and JWWA S 101. The requirements in question control the choice of the PVC-component used in the adhesive in regard to molecular weight and molecular weight distribution. For example, the so-called 60°C test in DIN 16 970 demands adequate thermal stability of the PVC material used for the adhesive. This thermal stability depends upon the material parameters mentioned above.

According to investigations conducted by Applicants, the performance and economic optimum of the PVC used in the adhesive for the PVC-adhesive compositions in question here lies at a K-value of 58 ± 1 and thus, on account of the solution behavior of this PVC material, requires a solvent composition which necessitates relatively high percentages of the above-mentioned cyclic PVC-solvents for formulating storable, "up-to-standard", gap-filling and creep-resistant adhesives. All attempts to displace the solvent composition in favour of non-cyclic components by reducing the K-value to below the specified limit were unsuccessful

because at least one of the four criteria mentioned above is not or no longer satisfied by the adhesive composition.

The teaching of the present invention is based on the surprising observation that a combination of PVC-types having different K-values leads to adhesive formulations of the type in question here which conform to standards and are storable, gap-filling and creep-resistant and, at the same time, to a significant reduction in the tendency towards stress crazing compared with known adhesive compositions of the type currently used in practice through a limitation of the content in the solvent mixture of the cyclic PVC-solvents mentioned above.

Accordingly, the present invention relates to compositions for bonding mouldings of rigid PVC based on a PVC-solution in a solvent mixture containing cyclic PVC-solvents which have PVC solids contents of from about 10 to 30% by weight. The new adhesive compositions are characterized in that they contain dissolved PVC having a K-value of 58 ± 1 in admixture with dissolved PVC having a K-value in the range from 45 to 52 for a content of cyclic PVC-solvents in the solvent mixture of no more than about 50% by weight, based on the weight of the adhesive as a whole. In one preferred embodiment, the following two PVC types in admixture with one another are present in solution in the new adhesive compositions:
PVC having a K-value of 58 ± 1 and PVC having a K-value of about 49 to 50.

In another preferred embodiment of the invention, the PVC-component having the K-value of 58 ± 1 makes up from about 40 to 85% by weight and more especially from about 45 to 60% by weight of the total weight of the dissolved PVC-types whilst the other component with the lower K-value correspondingly makes up from 60 to 15% by weight and, in the particularly preferred embodiment, from 55 to 40% by weight. It can be advisable to dissolve substantially

equal quantities by weight of the two PVC types in the solvent mixture.

One particular feature of the invention is that there is no need not to use known good PVC-solvents of cyclic structure, instead it is merely necessary to limit their content in the solvent mixture to achieve the required reduction in stress-induced corrosion. Thus, in one preferred embodiment of the invention, the mixture of PVC-solvents contains the cyclic solvents, more especially tetrahydrofuran and/or cyclohexanone, in quantities of from about 30 to 50% by weight and more especially in quantities of from about 35 to 45% by weight, based in each case on the total weight of the adhesive.

The remaining components of the liquid phase of the adhesive composition according to the invention are formed by non-cyclic PVC-solvents, among which non-cyclic ketones and, above all, methyl ethyl ketone are particularly important. In addition to these non-cyclic solvents, other non-cyclic PVC-solvents are used, generally in small quantities, in which case the use of limited quantities of dimethyl formamide can again be of particular significance.

Particularly preferred adhesive compositions according to the invention contain approximately 20% by weight of dissolved PVC-components of the type mentioned, from about 40 to 50% by weight of tetrahydrofuran and cyclohexanone, preferably mixed in a ratio of from about 1:1 to 2:1, and for the rest non-cyclic PVC-solvents, more especially about 25 to 35% by weight of methyl ethyl ketone and, for the rest, dimethyl formamide. The percentages quoted are all based on the total weight of the adhesive composition.

To prepare the adhesives according to the invention, the organic solvent is first introduced into a heatable tank equipped with a cooler. The PVC to be used in accordance with the invention is then introduced with stirring. The PVC is best introduced in an inert gas phase

(nitrogen). The temperature should be between about 20 and 80°C and preferably between 30 and 45°C. The mixture has to be stirred for about 1/2 to 2 hours in the preferred temperature range until a completely homogeneous solution is obtained.

Small quantities of filler, such as silica or insoluble silicates or even titanium dioxide, zinc oxide or the like may optionally be suspended with continued stirring, as known per se. If desired, small quantities of an organic dye may be added to the solvent at this stage or even from the outset to make the adhesive easier to recognize or identify. Fluorescers or optical brighteners may be used for this purpose. When all the constituents are dissolved or uniformly suspended, the adhesive is packed in transport containers. It may then be used without further storage.

The adhesives according to the invention do justice to the fact discovered by Applicants that the undesirable danger of stress-induced corrosion increases in the following sequence according to the solvent selected for the adhesive system: methylene chloride/dimethyl formamide/methyl ethyl ketone/tetrahydrofuran/cyclohexanone. Determination of the comparative figures for assessing the effect of the solvents in initiating stress crazing was carried out in two ways:

1. Determination of the brittleness temperature by impact testing (DIN 53 453) after solvent action

The test specimens used were standard small bars according to DIN 53 453 which were immersed for 5 minutes in the solvents mentioned below (20°C). Before the tests were carried out, the test bars dabbed with cotton wool were stored in air for 1000 hours at 20°C/60% relative humidity. The test specimens were cooled and subjected to the impact test at the temperatures shown.

The criterion is a 50% failure rate as a function of temperature after 1000 hours' desorption.

	Polyvinyl chloride	-52°C
	Methylene chloride	-38°C
5	Dimethyl formamide	-28°C
	Methyl ethyl ketone	-21°C
	Tetrahydrofuran	+12°C
	Cyclohexanone	+22°C.

- 10 2. Peak compressive strength on pipe sections after 168 hours' solvent absorption at -5°C followed by desorption for 1 hour at +20°C

The criterion is the failure or cracking rate at 30% compression, based on diameter:

15	Polyvinyl chloride	0%
	Methylene chloride	0%
	Methyl ethyl ketone	20% cracking
	Tetrahydrofuran	100% cracking

- 20 In formulations 1 to 9 below, No. 1 - a comparison example - is a standard commercial PVC-adhesive (Tangit: Henkel KGaA, Düsseldorf) of the type in question here which contains the basically optimal PVC-component having the K-value of 58 in dissolved form. The following Nos. 2 to 6 are also comparison examples and illustrate the results achieved in reducing the stress crazing level by methods other than the teaching according to the invention. Comparisons 2 to 6 show that in no case can all requirements, including the reduced danger of stress crazing, be satisfied.

- 30 Examples 7, 8 and 9 are intended to illustrate the teaching according to the invention, the required objective of combining all desirable properties being achieved in every case.

Experimental SectionComparison No. 1 (state-of-the-art)

	PVC K-value 85	20%	<u>Remarks</u>
	Tetrahydrofuran	50%	positive: up-to-standard, creep-resistant, gap-filling
5	Cyclohexanone	20%	
	Dimethyl formamide	5%	negative: danger of stress
	Methyl ethyl ketone	5%	crazing with a large excess of adhesive

10 Comparative tests to reduce stress crazing (2 to 6)Comparison No. 2

	PVC K-value 5.6	20%	<u>Remarks</u>
	Tetrahydrofuran	40%	positive: reduced danger of stress crazing
	Cyclohexanone	10%	
15	Dimethyl formamide	5%	negative: not up-to-standard, poor thermal stability
	Methyl ethyl ketone	25%	

Comparison No. 3

	PVC K-value 58	10%	<u>Remarks</u>
20	PVC K-value 50	10%	positive: up-to-standard, creep-resistant, gap-filling
	Tetrahydrofuran	50%	
	Cyclohexanone	20%	negative: danger of stress
	Dimethyl formamide	5%	crazing with a large excess of adhesive
	Methyl ethyl ketone	5%	

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Comparison No. 4a to c

PVC types having K-values of 50 (a), 58 (b) and 63 (c) were used:

	a)	b)	c)	<u>Remarks</u>
30	PVC-content 20	20	20%	positive: rel. low risk of stress crazing
	Methylethyl ketone	80	70 %	
				negative: not up-to-standard non-creep-resistant
35	Dimethyl form.	10	%	no storage life, poor

thermal stability

Methylene chloride 80%

Comparison No. 5

5	PVC K-value 63	10%	<u>Remarks</u>
	PVC K-value 50	10%	positive: reduced risk of stress crazing, gap-filling
	Tetrahydrofuran	40%	negative: not up-to-standard,
	Cyclohexanone	15%	no storage life
10	Dimethyl formamide	5%	
	Methyl ethyl ketone	20%	

Comparison No. 6

	PVC K-value 63	10%	<u>Remarks</u>
15	PVC K-value 46	10%	positive: reduced risk of stress crazing, gap-filling
	Tetrahydrofuran	30%	negative: not up-to-standard, no
	Cyclohexanone	15%	shelf life, poor thermal
	Methyl ethyl ketone	30%	stability
20	Dimethyl formamide	5%	

Examples according to the inventionExample 7

	PVC K-value 58	10%	<u>Remarks</u>
25	PVC K-value 50	10%	positive: up-to-standard, reduced
	Tetrahydrofuran	20%	risk of stress crazing,
	Cyclohexanone	20%	creep resistant, gap-filling
	Methyl ethyl ketone	35%	negative: -----
30	Dimethyl formamide	5%	

Example 8

	PVC K-value 58	16%	<u>Remarks</u>
	PVC K-value 50	4%	positive: up-to-standard, reduced
35	Tetrahydrofuran	20%	risk of stress crazing,

Cyclohexanone 20% creep resistant, gap-filling

Methyl ethyl ketone 35% negative: -----

Dimethyl formamide 5%

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Example 9 (adhesive according to the invention)

PVC K-value 58 10% Remarks

PVC K-value 50 10% positive: up-to-standard, reduced

Tetrahydrofuran 35% risk of stress crazing,

10 Cyclohexanone 15% creep resistant, gap-filling

Methyl ethyl ketone 25% negative: -----

Dimethyl formamide 5%

15 The technical evaluation of product quality is based on DIN 16 970. This standard sets out internal pressure creep tests of at least 1000 hours' duration both at room temperature and also at 60°C taking into account a negative gap of -0.2 mm and a positive gap of +0.6 mm. The measurements were carried out with a gap of +0.6 mm at 20°C/51 bar and at 60°C/16 bar.

20 It also stipulates a minimum compressive shear strength of 7 N/mm² at -0.2 mm and 5 N/mm² at +0.6 mm gap. The measurements were carried out at 20 to 22°C.

25 In the evaluation of the properties of the adhesive mixtures, particularly the experimental data, it was found that compositions 4, 5 and 6 were not stable in storage and were therefore unsuitable for practical application. Compositions 1 and 3 gave bonds which, although having good strength values (compressive shear strength, internal pressure creep strength), had a distinct tendency to crack under stress. In addition to the disadvantages of 1 and 3, composition 2 also showed inadequate heat resistance.

30 Compositions 7, 8 and 9 according to the invention showed the following compressive shear strengths in the

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series test (six samples in each case):

11.5 to 11.9 N/mm² at -0.2 and

8.1 to 8.4 N/mm² at +0.6.

5 The internal pressure creep strength was measured at a positive gap of 0.6 mm at 20°C/51 bar and also at 60°C/16 bar. In every case creep strengths equivalent to more than 1000 hours were measured.

Accordingly, there was no evidence of stress-induced corrosion under severe stressing.

CLAIMS

1. A composition for bonding mouldings of rigid PVC based on a PVC-solution in a liquid solvent mixture containing cyclic PVC-solvents for PVC-solids contents of from about 10 to 30% by weight, characterized in that it contains dissolved PVC having a K-value of 58 ± 1 in admixture with dissolved PVC having a K-value of from 45 to 52 for a content of cyclic PVC-solvents in the solvent mixture of no more than about 50% by weight, based on the weight of the adhesive.
2. An adhesive as claimed in claim 1, characterized in that the dissolved PVC-component having the lower K-value has a K-value in the range from about 49 to 50.
3. An adhesive as claimed in claims 1 and 2, characterized in that it contains the PVC types with the different K-values mixed in the following proportions (% by weight, based on the total weight of the dissolved PVC-types):
- K-value 58 ± 1 : 40 to 85, preferably 45 to 60
- K-value 45 - 52: 60 to 15, preferably 55 to 40.
4. An adhesive as claimed in claims 1 to 3, characterized in that the solvent mixture contains the cyclic PVC-solvents, more especially tetrahydrofuran and/or cyclohexanone, in quantities of from about 30 to 50% by weight and preferably in quantities of from 35 to 45% by weight, based in each case on the total weight of the adhesive.
5. An adhesive as claimed in claims 1 to 4, characterized in that, in addition to the limited amount of cyclic solvents, the liquid solvent mixture contains non-cyclic ketones, more especially methyl ethyl ketone, preferably in admixture with small quantities of dimethyl formamide.



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