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(54) Title: FLEXIBLE PVC MATERIAL CONTAINING GLYCIDYL ACRYLATE, WITH HIGH RESISTANCE TO HEAT AGEING, METHOD AND USE

(57) Abstract

A procedure for preventing a reduction of flexibility in a material containing vinyl chloride after ageing at high temperature, a thermoplastic material and an application of this material. A polymer mixture is used containing 20-100 weight % of a copolymer consisting of 80-99.9 weight % VCM and 0.1-10 weight % acrylate containing glycidyl, 0-80 weight % PVC and 0-80 weight % of other copolymers based on at least 70 % VCM. The material is specially suited for vehicle cables, hoses, seals and packings.

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Flexible PVC material containing glycidyl acrylate, with high resistance to heat ageing, method and use

The present invention concerns a procedure for preventing the reduction of flexibility of a plasticised material containing vinyl chloride after ageing at high temperature, a thermoplastic material containing vinyl chloride and an application of this material.

For individual areas of use such as, for example, for cables for application in the transport industry, one of the most important requirements is that the cable retain as much of its flexibility as possible after ageing at warm temperatures. According to the French standard for vehicle cables, NFR 13-415, a cable must tolerate fatigue tests carried out at -25°C after thermal ageing. For a type 3 cable in accordance with this standard, which is used in the engine room, among other places, the thermal ageing is carried out at 155°C for 240 hours.

According to Volvo's standard STD 7611,13 class 3, a cable must be able to withstand ageing at 170°C for 6 hours, and at 120°C for 1000 hours and then pass a cold bending test at -30°C.

It is thus important that the cables retain as much of their flexibility as possible after ageing. This is emphasised by the fact that the more flexibility a cable retains after ageing, the more rigid it can be made, which is of advantage for many of the other tests within the scope of the standard, such as, for example, the deformation test under heat, resistance to chemicals and resistance to wear.

It is difficult to find insulating materials which satisfy these requirements and the requirements of other standards for flexibility after ageing at a reasonable price and which do not require additional processing.

Polyvinyl chloride is a material which is easy to process and is relatively reasonably priced. However, PVC materials which are exposed to ageing at high temperature become more brittle on account of the fact that the material is broken down combined with a reduction in plasticiser. The loss of plasticiser means that there is a certain connection between the weight loss and the flexibility.

The object of the invention is thus to produce a material containing vinyl chloride which is flexible after ageing at high temperature. It is of special interest to produce materials which can be used in cables, particularly vehicle cables, hoses, seals and packings.

This is achieved by means of the procedure, product and use described below and the invention is described in more detail in the enclosed claims.

With this invention we have arrived at a method which makes it possible to use a plasticised thermoplastic material containing vinyl chloride at higher operating temperatures than possible for material based on a PVC homopolymer. The material has all the positive properties which such a material possesses such as good processing properties, good dyeing properties, good stripping properties, adapted flexibility, good printing possibilities, good resistance to chemicals etc.

The invention consists in wholly or partly replacing PVC with a copolymer based on VCM and small parts of glycidyl-containing comonomers such as glycidyl acrylate, glycidyl methacrylate or glycidyl butacrylate. It is preferred to use glycidyl-containing comonomers in a quantity of 0.1-10 weight %. The thermoplastic PVC material, which has good flexibility after ageing at high temperature, consists of polymer, plasticiser, thermostabiliser and other additives. The material contains 20-100 weight % of one copolymer in which the monomer consists of 80-99.9 weight % of VCM and 0.1-10 weight % of glycidyl-containing acrylate, and 0-80 weight % of other copolymers based on at least 70 % VCM. If required, the glycidyl-containing polymer may contain up to 10 weight % of another monomer such as, for example, vinyl acetate and acrylates which do not contain glycidyl such as methyl methacrylate, ethyl methacrylate and butyl methacrylate.

Common plasticisers suited to PVC are used. The plasticiser is added in a quantity of 20-100 phr (phr = parts per 100 parts of polymer). It may also be possible to use polymers such as, for example, EVA (copolymer between ethene and vinyl acetate) or polyadipate as a plasticiser in such mixtures. Small quantities of other polymers can be added such as, for example, chlorinated polyethene, EVA, a terpolymer between ethene, vinyl acetate and carbon monoxide, EBA (a copolymer between ethene and butyl acrylate), polyadipates and nitrile rubber without the material losing its properties. The material is well suited for use in cables, particularly vehicle cables, hoses, seals and packings.

The invention will be explained in more detail in the following examples. In the examples the quantities are given in phr.

Tests

The cold-flex according to Clash and Berg (ISO 547) was measured in samples which had not been aged and in samples which had been aged for 240 hours at 155°C. The cold-flex measures the temperature at which a sample strip of approximately 1 mm thickness has a flex modulus of 310 MPa. The lower the temperature indicated, the more flexible the sample. The reduction in weight was measured as a comparison between the sample's weight before and after ageing for 240 hours at 155°C.

Example 1

The following formulations were mixed in a small mixer at up to 110°C. They were then rolled at 170°C for 5 minutes and subsequently pressed at 190°C for 5 minutes. The pressed samples were aged in a cell furnace at 155°C for 240 hours.

TABLE 1

Formulation	A1	A2	A3
PVC homopolymer	100	-	-
Copolymer VCM:GMA 99:1	-	100	-
Copolymer VCM:GMA 98:2	-	-	100
Linear trimellitate[1]	50	50	50
Stabiliser/lubricant mix[2]	8	8	8
Oxidised polyethene wax[3]	0.1	0.1	0.1

[1] Softener for high-temperature applications

[2] Commercial stabiliser/lubricant mix based on tetrabasic lead sulphate

[3] Lubricant

The results are shown in table 2:

TABLE 2

Formulation	A1	A2	A3
Cold-flex, non-aged sample (°C)	-20	-20	-21
Cold-flex, aged sample (°C)	-9	-14	-19
Weight loss (%)	6.5	3.1	3.4

Table 2 shows that when PVC (homopolymer based on VCM) is replaced with a copolymer based on VCM and small parts of GMA, a material is obtained which tolerates ageing at high temperatures considerably better. While mixture A1, based on a homopolymer, has a 6.5 % weight loss after ageing at 155°C for 240 hours, mixtures A2 and A3, based on copolymers, have weight losses of about half of this. Mixture A1 loses approximately 12°C in cold-flex on account of ageing while A2 and A3 lose 6°C and 2°C respectively.

This effect is clearly unexpected as the thermostability for the pure polymers, without additives, is poorer for copolymers than for the homopolymer.

Example 2

In order to investigate whether the effects in example 1 could have been achieved by other means than by replacing the polymer, tests were carried out with increased quantities of thermostabiliser, added epoxidised soya bean oil and added antioxidant. The formulations are shown in table 3.

TABLE 3

Formulation	A1	A4	A5	A6
PVC homopolymer	100	100	100	100
Linear trimellitate	50	50	50	50
Stabiliser/lubricant mix	8	10	8	8
Oxidised polyethene wax	0.1	0.1	0.1	0.1
Epoxidised soya bean oil[4]	-	-	3	-
Antioxidant	-	-	-	0.2

[4] Auxiliary stabiliser with glycidyl groups

Table 4 shows the measurements carried out on the formulations indicated in table 3.

TABLE 4

Formulation	A1	A4	A5	A6
Cold-flex before ageing (°C)	-20	-20	-23	-22
Cold-flex after ageing (°C)	-9	-3	-7	-10
Weight loss (%)	6.5	8.0	7.2	6.9

Table 4 shows clearly that the effect of improved flexibility after ageing cannot be achieved by increasing the quantity of stabiliser. On the other hand it was shown that an increased quantity of lead stabiliser gave rise to poorer flexibility after ageing. One possible cause of this might be that the lead stabiliser contributes to splitting and thus the reduction in softener. The addition of epoxidised soya bean oil or antioxidant did not produce the required effect either.

The weight loss for the materials A1, A4, A5 and A6 in tables 3 and 4 is obviously greater than for mixtures A2 and A3 which contain the copolymer VCM:GMA. In addition, the cold-flex value is considerably worse for all the materials in tables 3 and 4 in comparison with A2 and A3.

Example 3

A test was carried out replacing the plasticiser trimellitate in the formulations A1 and A2 with a softener of the phthalic type, diundecylphthalate (DUP). The formulations are shown in table 5.

TABLE 5

Formulation	B1	B2
PVC homopolymer	100	-
Copolymer VCM:GMA 99:1	-	100
DUP	40	40
Stabiliser/lubricant mix	8	8
Oxidised polyethene wax	0.1	0.1

The results are given in table 6.

TABLE 6

Formulation	B1	B2
Cold-flex before ageing (°C)	-12	-12
Cold-flex after ageing (°C)	-3	-9
Weight loss (%)	11.1	6.8

The results in table 6 are similar to the results given in table 2. Replacing the PVC homopolymer with the copolymer VCM:GMA 99:1 gives clearly improved ageing properties. The weight loss in connection with ageing is less and the flexibility deteriorates much less than with ageing when the copolymer is used.

Example 4

The stabiliser which is normally recommended for applications with extreme heat stress is dibasic lead phthalate. Comparative studies were therefore carried out with formulations with this type of stabiliser, see table 7.

TABLE 7

Formulation	C1	C2	C3
PVC homopolymer	100	-	-
Copolymer VCM:GMA 99:1	-	100	-
Copolymer VCM:GMA 98:2	-	-	100
Linear trimellitate	50	50	50
Dibasic lead phthalate	7	7	7
Ca-stearate[5]	1	1	1

[5] Lubricant

The formulations in table 7 were aged at 155°C for 240 hours and the following results achieved as shown in table 8.

TABLE 8

Formulation	C1	C2	C3
Cold-flex before ageing	-21	-20	-22
Cold-flex after ageing (°C)	-10	-13	-15
Weight loss (%)	8.2	4.7	5.9

Even in this case it was shown that the copolymers VCM:GMA 99:1 and 98:2 respectively (C2 and C3) are far superior to the formulations containing the homopolymer PVC (C1). The cold-flex deteriorated considerably less after ageing for C2 and C3 and the weight loss was also less.

With the present invention a method has been found for producing formulations of a PVC type which have better tolerance to ageing at high temperatures than normal PVC formulations.

Patent claims

1. A procedure for preventing a reduction of flexibility for plasticised materials containing vinyl chloride after ageing at high temperature,
characterised in that a copolymer of vinyl chloride and a monomer containing glycidyl are used.

2. A procedure in accordance with claim 1,
characterised in that glycidyl acrylate, glycidyl butacrylate or glycidyl methacrylate are used as the comonomer containing glycidyl.

3. A procedure in accordance with claim 1,
characterised in that the comonomer is added in a quantity of 0.1-10 weight %.

4. A procedure in accordance with claim 1,
characterised in that 20-100 weight % copolymer of VCM and acrylate containing glycidyl, 0-80 weight % of PVC and 0-80 weight % of other copolymers based on at least 70 % VCM are used.

5. A thermoplastic PVC material with good flexibility after ageing at high temperature, consisting of polymer, plasticiser, thermostabiliser and other common additives,
characterised in that the material contains 20-100 weight % of a copolymer in which the monomer consists of 80-99.9 weight % of VCM and 0.1-10 weight % of acrylate containing glycidyl, 0-80 weight % of PVC and 0-80 weight % of other copolymers based on at least 70 % VCM.

6. A thermoplastic material in accordance with claim 5,
characterised in that the acrylate containing glycidyl is glycidyl acrylate, glycidyl butacrylate or glycidyl methacrylate.

7. A thermoplastic material in accordance with claim 5, characterised in that the material may contain up to 10 % of another monomer such as vinyl acetate and acrylates not containing glycidyl.

8. A thermoplastic material in accordance with claim 5, characterised in that the material may contain other polymers such as, for example, chlorinated polyethene, EVA, a terpolymer between ethene, vinyl acetate and carbon monoxide, EBA, polyadipates and nitrile rubber.

9. The use of a thermoplastic PVC material consisting of at least 20 % of a copolymer in which the monomer consists of 80-99 weight % of VCM and 0.1-10 weight % of acrylate containing glycidyl for materials which need to be flexible after ageing at high temperature.

10. The use of the material in accordance with claim 8 for vehicle cables, hoses, sealing strips or packings.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 93/00062

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C08L 27/06, C08F 214/06
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)

IPC5: C08L, C08F

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

SE,DK,FI,NO classes as above

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

DERWENT WORLD PATENTS INDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP, A2, 0264916 (UNION CARBIDE CORPORATION), 27 April 1988 (27.04.88), claims 1, 7 and 8 --	1-10
X	EP, A2, 0358067 (BASF AKTIENGESELLSCHAFT), 14 March 1990 (14.03.90), abstract --	1-10
X	EP, A1, 0389208 (NIPPON ZEON CO., LTD.), 26 Sept 1990 (26.09.90), see example 3 --	1-10
A	EP, A2, 0481325 (THE B.F. GOODRICH COMPANY), 22 April 1992 (22.04.92) -- --------	1-10

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0264916	27/04/88	AU-B- 600529	16/08/90
		AU-A- 7994087	21/04/88
		CA-A- 1302004	26/05/92
		JP-A- 63183906	29/07/88
		US-A- 4970127	13/11/90
EP-A2- 0358067	14/03/90	DE-A- 3829711	22/03/90
		JP-A- 2163107	22/06/90
		US-A- 4968763	06/11/90
EP-A1- 0389208	26/09/90	JP-A- 2248348	04/10/90
EP-A2- 0481325	22/04/92	AU-A- 8565991	30/04/92
		JP-A- 4264150	18/09/92