Translated by Paula Raizman

Prevention or lowering of damages resulting from the evolution of hydrogen chloride during fires of halogen-containing resins. Oelenheinz, K. (Sueddeutsche Kabelwerke Zweigniederlassung der Vereinigte Deutsche Metallwerke A.-G.) Ger. Offen. 1,921,773 (February 5, 1970, Austrian Appl. May 21, 1968; 17 pp.)

This invention concerns a process for the prevention or lowering of damages caused by evolution of hydrogen chloride in the burning of halogen-containing resins by using hydrogen halogen-binding agents.

Hydrogen halide is released during burning of X-containing resins (X - halogen), and because of its corrosive action, particularly in combination with water, leads to considerable damages, far above the harm done by fire. These damages consist not only in the corrosion of metal parts, machines and similar installations, but also in the attack by these acid vapors on portions of buildings, particularly steel enclosures in the foundations, on which is based the stability of the building. These acid vapors render difficult fighting of such fires and even in cases of early extinction, there remains in the portions of buildings burned a dilute, in water dissolved acid, which is hard to remove.

Halogen-containing resins are considered difficultly flammable because of the high amount of halogen. However, already under the influence of light or relatively low temperatures these resins give off hydrogen chloride. This is particularly valid for PVC. As this hydrogen halide catalyzes further evolution of hydrogen halides, the resin is finally destroyed, while undergoing color changes from yellow to black. This influence is accelerated by the effect of other factors, such as oxygen, or impurities such as traces of metals and water. It is known that halogen-containing resins, as for example PVC, should be treated after their preparation with dilute alkali or alkaline reacting solutions, such as sodium hydroxide, ammonia or sodium carbonate in order to obtain products stable to light and heat (Ger. Pat. 659,042, 663,220).

It is also known that addition of stabilizers to X-containing resins prevent the splitting off of hydrogen halide during processing and in normal use. The simplest agent is the addition of alkalis, such as alkaline hydroxides or carbonates or of amines (Ger. Pat. 749,509). In Ger. Pat. 701,837 the addition of aromatic compounds with a hydroxyl group in ortho position to a nitro-, alkyl- or carboxylic ester group was advised. Others proposed the addition of lead or silver or their oxides, hydroxides or carbonates (Ger. 729,419), or of natural aromatic amino acids (Ger. 724,524) or of a mixture of alkali-active compounds and amines or carbamides (Ger. 746,081). Among the more recent stabilizers are alkali phosphates, calcium-,

strontium, barium or lead compounds, and also ones based on cadmium, zinc and tin (G. Schulz, Plastics, 1964 p. 297-99).

All these known additives are not capable to bind the spontaneously formed large amounts of hydrogen halide in case of a fire, and to prevent the resulting corrosion. The proposed alkaline compounds, such as alkali hydroxides or carbonates, do not release under the influence of heat volatile alkaline compounds. The proposed organic compounds are mainly burned to H_2O and CO_2 without splitting off acid-binding components. Even such stabilizers as alkali phosphates or other metal-containing compounds do not have the ability to bind the large amounts of hydrogen halide formed at higher temperatures and above all do not form at fire-temperatures volatile vapors, which could mix with the halogen vapors and render them non-damaging by formation of harmless compounds.

This invention deals with the reduction or prevention of losses resulting from hydrogen halides formed by burning of halogen-containing resins.

This consists in the addition to the resins of such compounds which release at burning temperature volatile compounds capable of binding the hydrogen halide formed.

X-containing resins are resins containing halogen in any form. To them belong PVC, P-vinylidene chloride, chlorinated rubber, chlorinated polyether, polytetrafluoroethylene, polytrifluoroethylene, their mixed polymers with other monomers and such mixtures as graft polymers. This invention concerns also halogen-free resins to which X-containing compounds were added, such as chloroparaffins as plasticizer, pentachlorophenol as preservative, bromocompounds to render them difficult to burn, and also X-containing dyes and pigments.

According to this invention the split off volatile halogen compounds are organic or inorganic or a mixture of both.

To these compounds are added others which either facilitate the splitting off of the X-containing compounds, or accelerate or catalyze it.

The nature and amount of the halogen-binding compound added is sufficient to unite with the volatile hydrogen halides formed at burning temperatures.

As volatile given off halogen-binding compounds in the sense of this invention are compounds which split off alkaline reacting compounds. To them belong NH_4CO_3, NH_4HCO_3, $(NH_4)_3PO_4$, $NH_4H_2PO_4$, $(NH_4)_2SO_4$, NH_4HSO_4, primary, secondary and tertiary amines, mono- and polyamines, such as hexamethylenediamine, mono-, di- and trimethyl derivative of ammonium hydroxides, amides and diamides such as urea and thiourea, acetamide, N-methylamide, cyclic amides, imides such as guanidine, oximes

and compounds splitting off hydroxylamine or hydrazine under heat. All these compounds bind hydrogen halides or give off such binding compounds.

These alkaline compounds contain preferably nitrogen and hydrogen, where nitrogen can be in a main or secondary chain or in a cycle and substituted with hydrogen, which can be completely or partially replaced by other atoms or radicals. Such compounds are ammonia, its salts and derivatives, primary-, secondary- and tertiary-amines or quaternary ammonium compounds, with substituents such as hydroxyl-, alkyl- or aryl-groups.

To facilitate, accelerate or catalyze the dissociation of volatile hydrogen halide-binding compounds metal oxides are added, such as calcium-, magnesium-, barium-, zinc, iron-, aluminum- and titanium oxides.

This procedure applies when from the X-containing resins products with technological properties were made, and their value is lowered by the addition of HX-binding compounds. In this case the above compounds should be added only to products with small or no technological value.

These volatile released HX-binding compounds should be added to the final products such as foils, sheets, covers etc., containing a binder. These compounds, giving up the volatile, HX-binding compounds, can also be added to the halogen-containing resins or to their masses, or their semifinished or final products in the proper proportions in the form of small balls, bags, pouches etc.

By using this invention it is possible to prepare numerous technically important products.

A covering prepared according to this invention and characterized by the addition of compounds splitting off volatile, halogen halide-binding compounds, have an outer or upper layer containing little or not all of the latter and one or more inner or lower layers containing high or rising amounts of these volatile substances.

In fig. 2 is represented such a covering consisting of an upper layer 9, with little or none of the named compound, maintaining in this manner the required technological properties, such as grinding stability or hardness, and a layer 10 between this one and the basic layer 11, from which no particular mechanical properties are required and which can therefore contain high amounts of these compounds.

Electric cables prepared according to this invention with a partial or total isolation or protection by halogen-containing compounds is characterized by the addition of hydrogen-halide splitting off compounds. The outer cover or isolation possess little or not at all of the above compounds and one or more of the inner layers, contain high or rising amounts of the latter.

Fig. 3 represents the cross-cut of an electric cable, in which the electric conductor 15 is surrounded by isolation 14 which does not contain or contains little of the above compounds in order to maintain the isolation properties. These are surrounded by an intermediary layer 13, which only serves to fill out the proof cock and outer roundness of the mutually connected conductor 15 and therefore can be rich in the above compounds without lessening the properties of the cables. The whole is surrounded by an outer protective shell 13, which again does not contain or only little of these compounds, so that the required technological properties can be maintained.

Also tubes or pipes which are partially or totally made from halogenated resins can be produced by this invention. They are characterized by the addition of compounds giving off volatile hydrogen halides in which these compounds are added in various amounts or only partially to the pipes.

Fig. 4 shows a tubing or a pipe consisting of an inner layer 18, without the above compounds, so that the stability against the flowing medium be maintained, an intermediary layer 17, which can be rich in the above compounds, because no particular technological properties are required from it, and an exterior layer 16, which does not contain or only so much of these compounds, as to maintain the necessary properties such as abrasion stability and viscosity.

The compounds of this invention can be mixed with other fire-fighting means.

The following examples will illustrate the invention.

Examples 1 to 12.

The following halogen-containing polymer mixture was used for examples 1 to 1:

67.0 wt. parts of PVC
29.0 " " " dioctyl phthalate
3.5 " " " tribasic lead sulfate.
0.5 " " " 28% lead stearate.

To this basic mixture were added the compounds of this invention or their mixtures in finely powdered form, and the whole thoroughly blended.

Testing of the effect of these compounds is represented in fig. 1:

1 - is a pressure flask, 2 - a conductor, 3 - the first washing flask as counter of bubbles, 4 - a pipe from hard-melting glass, 5 - a ground joint for the studied compounds, 6 - a Bunsen burner, 7 - a second washing flask with an indicator, 8 - a third washing flask with an indicator.

After connecting an air flow which passes through the pressure flask 1 conductor 2 and in water-containing, bubble counting 3 and finally through the entire apparatus, in pipe 4 the compound present in 5 is burned with 5 and the formed gases and vapors are passed through both washing flasks containing an aqueous indicator

solution. A mixture according to Yamada serves as indicator. The coloration at pH values changes from 4 - to red, 5 - to orange, 6 - to yellow, 7 - to green, 8 - to blue, 9 - to indigo, 10 - to purple. The ratios of the added compounds and results are given in the following table:

Sample	Addition to 150 g PVC-mixture				Metalloxid			Result*)
	Dicyandiamid	Harnstoff	Ammonsulfat	Sek.Ammonphosphat	MgO	ZnO	TiO_2	
1	70	-	50	-	20			good
2	35	-	25	-	10			bad
3	-	-	50	-	20			bad
4	-	-	100	-	40			bad
5	-	70	50	-	20			good
6	70	-	-	50	20			good
7	-	70	-	50	20			good
8	35	35	25	25	20			good
9	26,5	26,5	19	19	15			good
10	16,6	16,6	14,3	14,3	11,3			bad
11	-	70	50	-	-	35		good
12	-	70	50	-	-	-	35	good

*) good - complete binding of the Br-gases.
bad - incomplete binding of the Br-gases.

The best results obtained with samples 1,5,6,7,8,9,11,12. In this case no formation of acid gases or vapors was found.

In a further control test example 1 was repeated and the gases leaving pipe 4 were led into two 1-liter round flasks connected to 7, containing about 20 mm of distilled water and conventional iron nails. In this test after 60 minutes there was no change on the surface of the nails,at the most a slight color formation.
In the blind test, without addition of the compounds, the nails were completely rusted within 60 minutes as a result of acid formation.

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Example 13

The following halogen containing polymer mixture was prepared,

41.0 wt parts PVC
19.0 " " dioctylphthalate
8.0 " " chloroparaffin
28.0 " " chalk
0.5 " " Pb-stearate
3.5 " " Pb-sulfate

carefully mixed and from mixture (1) was prepared a 1 mm thick film and rolled over a film of the following (2) composition:

21.0 wt parts butyl rubber
37.5 " " urea
26.8 " " ammoniumphosphate
0.5 " " stearic acid
3.5 " " paraffin
10.7 " " magnesium oxide

Samples were cut from these films for tests. The rods tested contained 2.44 g of the halogen-containing polymer mixture (1) and 1.87 g of additive (2).

The tests made similarly to examples 1 to 12 showed that even in rest-free burning no acid products were formed or the formed acid products were completely bound by the gases formed by the decomposition of urea or ammonium salts.

Even so the described control test, introduction of the vapors into a round flask filled with nails was repeated with a positive effect.

The advantages obtained here consist in the complete binding of the volatile hydrogen halides formed under the influence of higher temperatures from the halogen-containing polymers. In this way damages caused by these gases are prevented. Considering the great role the halogen-containing polymers play in the construction of dwellings and storehouses, this result represents a great economical interest and value.

Claims

1. Process for the prevention or reduction of the damages resulting from hydrogen halides in the burning of halogen-containing materials in which to the latter prior or during its preparation to a final product are added compounds which at temperatures of fires release volatile hydrogen-halides binding compounds.

2. Process according to claim 1 when this additive is added to the finished product.

3. Process according to claim 1 or 2, in which these compounds are inorganic or organic compounds or a mixture of both.

4. Process according to claims 1 to 3, in which to these volatile HX-releasing compounds are added others facilitating, accelerating or catalyzing this release.

5. Process according to claims 1 to 4, in which the nature and amount of the hydrogen halogen-releasing compounds are added in amounts sufficient for uniting with the formed hydrogen halides.

6. Process according to claim 2, in which the volatile, hydrogen halide releasing compounds are added to the semi-final or final products such as films, sheets, covers or other, preferably with a binder, cemented, welded or mechanically bound according to case.

7. Process according to one or the other of claims 1 to 6 in which the compounds releasing the volatile HX-binding compounds are added to the semi-final or final products in proper proportions in the form of small balls, bags, pouches or similar forms.

8. Process according to one of the claims 1 to 7, in which the compounds release volatile alkaline reacting compounds.

9. Process according to one of the claims 1 to 8, in which the alkaline compound contains nitrogen and hydrogen, where the nitrogen is present in the main or side chain or in a cycle and is substituted partially or totally with hydrogen, which can be replaced by other atoms or radicals, such as ammonia or its salts or derivatives such as primary, secondary or tertiary amines or quaternary ammonium compounds.

10. Process according to one or more claims from 1 to 9, in which the metal oxides facilitating, accelerating or catalyzing the release of volatile HX-binding compounds are added.

11. An installation, consisting partially or totally of X-containing polymers characterized by the addition of compounds splitting off volatile HX-binding compounds according to claims 1 to 10.

12. Cover according to claim 11 containing an outer or upper layer containing little or no compounds releasing volatile HX-binding gases, and one or more inner or lower layers containing high or rising amounts of the above compounds.

13. An electric cable with a partial or total isolation or protection cover of X-containing resins, to which are added the above compounds according to claims 1 to 10.

14. An electric cable according to claim 13, whose isolation or protective covers contain little or no compounds releasing HX and which contains one or more layers, particularly for the filling of the proof cork volumes, made from compounds releasing HX-binding materials.

15. Pipes or tubing, consisting partially or totally from halogen-containin resins, to which are added compounds splitting off volatile HX-binding ones according to claims 1 to 10.

16. Pipes or tubes according to claim 15, consisting of several layers, to which the compounds splitting off volatile HX-binding compounds are added in different ways to one or all layers.

17. Use of the compounds releasing HX-binding compounds according to claim 3 or 4 for the fighting of fires of X-containing resins, together with other fire-fighting means.

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Fig. 1

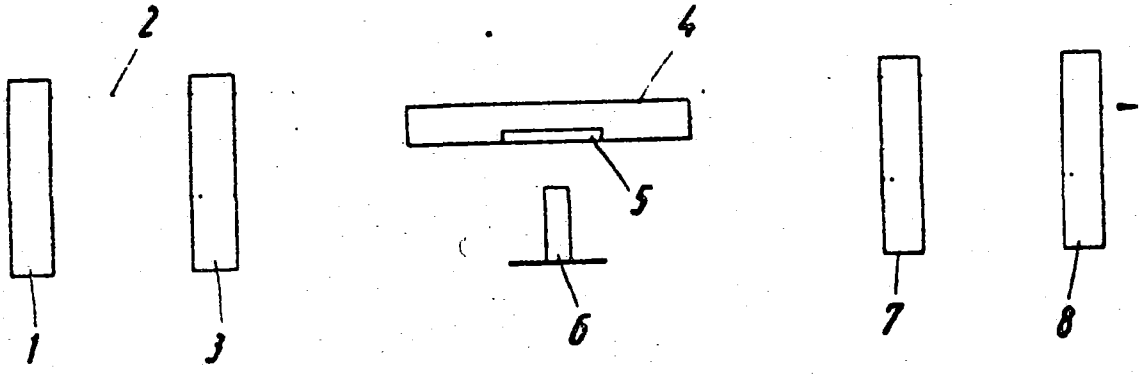

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Fig. 2

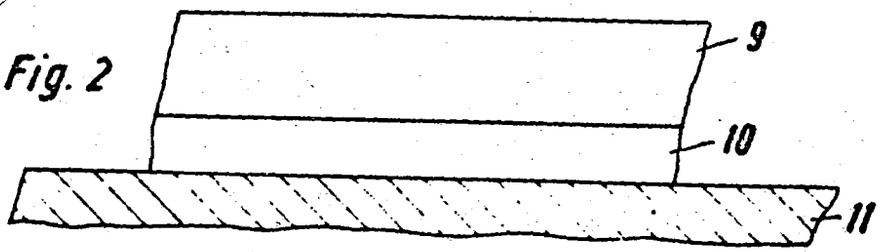

Fig. 3

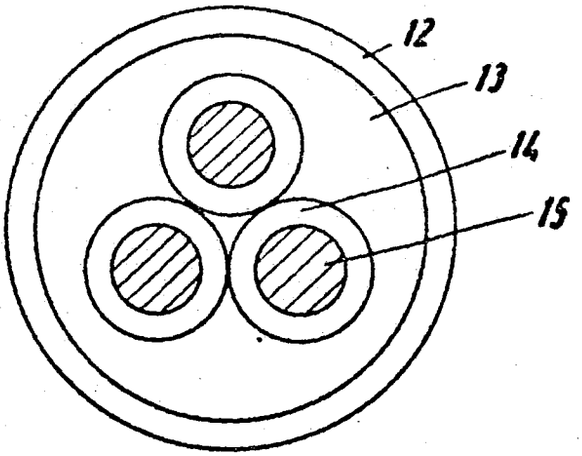

Fig. 4