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(19)

(54) IMPROVEMENTS IN AN INHIBITOR COATING FOR SOLID ROCKET PROPELLENT CHARGE

(71) We, WERKZEUGMASCHINEN-FABRIK OERLIKON-BUHRLE AG, a Company organised and existing under the laws of Switzerland of Birchstrasse 155, CH-8050 Zurich, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to a new and improved inhibitor coating solid propellent charges for protecting against undesired burning-off, the inhibitor coating being of the type comprising an insulating layer containing a binder and a filler and a protective- and adhesion layer which is located between the insulating layer and the propellent charge.

Inhibitor coatings of this type are known to the art by means of which there is covered a portion of the surface of the propellent charge in order to protect such surfaces against undesired burn-off. This measure is necessary when the rocket propellent charges are freely exposed within the rocket combustion chamber, especially when the propellent charge is constructed as an internal burner or an end burner. In both cases the effective burning surface of the propellent charge is determined by the reliable insulation of the remaining surfaces of the propellent charge. An undesired burn-off of burning-off at such insulated surfaces owing to detachment or failure of the insulating layer leads to ballistic malfunctions or tearing-down of the rocket and must be prevented.

The following requirements are placed upon the quality of the inhibitor coating or covering:

(a) The coating must be capable of withstanding temperature fluctuations in a range between −40° C to +60° C, i.e. it is either elastic or it possesses the same coefficient of expansion as the propellent charge.

(b) The coating must be capable of withstanding the mechanical and thermal loads during the burn-off, for instance, the acceleration forces during the flight of the rocket.

(c) The coating must be capable of being removed in as gaseous state as possible during the burning-off, since large proportions of carbon black particles or other solid particles lead to the pronounced formation of smoke, something which must be absolutely avoided in the case of wire-guided rockets.

(d) The coating must not decompose or disintegrate into larger pieces or parts, since otherwise such parts can clog the nozzles.

These prior art inhibitor coatings can contain:

(a) an organic binder formed of plasticized or non-plasticized plastomeric polymers.

(b) inorganic or organic fillers,

(c) fabrics formed of polymeric organic or inorganic substances, for instance formed of polyesters or glass which can be wound about the propellent charge.

These inhibitor coatings are applied by immersing the propellent charge in an insulating bath, by coating, by pressing-on, casting or by adhesively bonding skins or hides. The momentarily employed manufacturing technique is dictated by the composition of the binder.

(a) Coatings containing plastomeric binders, e.g. ether and ester derivatives of cellulose can only be applied in a dissolved state as a lacquer by immersion, coating or spraying.

(b) There can be only applied relatively thin layers, so that there are necessary the application of a number of layers and hence there must be carried out a number of working operations or steps because between the working steps there must take place each time a drying and removal of the solvent.

(c) The migration of the plaiicizer cannot be prevented, so that over prolonged periods of time the coating is softened and impaired in its effectiveness.

(d) The winding of foils about the propellent charge, and which foils have been imbued with the aforementioned lacquer, is cumbersome. When adhesively binding skins or

hides the danger exists that such will not adequately adhere at localized regions, particularly at the seam.

(e) Filled or unfilled coatings with elastomeric binders such as, for instance, polyurethanes, unsaturated polyesters or polyepoxides must be processed within the so-called "pot life", i.e. at the beginning of the hardening phase. Such coatings can only be applied by casting or pressing-on. The technique of pressing-on the coating is associated with the drawback that the working speed is small.

Accordingly the present invention provides a solid rocket propellant charge protected against undesired burning off by an inhibiting coating comprising a protective and adhesion layer and a castable insulating layer for protecting said propellant charge against undesired burning off, said protective and adhesion layer being located between the insulating layer and the propellant charge and consisting of a completely hardened polyisocyanate forming a barrier against plasticiser migration, said castable insulating layer containing a binder and a filler, the binder consisting of a castable mass which has low smoke developing properties in order to avoid clogging of the rocket nozzles and reduce visibility, the filler consisting of a cooling agent which is composed of a granular material having a grain size less than 150 microns, and the grain size is adjusted such that there is attained a packability of at least 55 percent by volume, the packability being designated by the symbol P which is the quotient of the solid density ψ in grams/cm^3 and the shaking density ψR in grams/cm^3, wherein:

$$P = \frac{\psi R}{\psi}$$

The present invention also provides a method of producing a solid rocket propellant charge protected against undesired burning-off by an inhibiting coating wherein said method includes preparing the insulating layer by admixing, in a kneader, a pre-adduct, a cooling agent, and an aromatic diamine, and either an aliphatic plasticizer or an aliphatic polyol, mixing being continued until the pre-adduct and diamine have completely reacted.

The casting technique requires mixtures possessing good flow properties. This requirement is fulfilled by means of the binder which is used, and due to the limitation of the largest possible proportion of a fine grain filler possessing high packability. However, this limitation is advantageously compensated by the advantages prevailing when employing casting techniques, to wit, high production speeds, simplicity of the method.

Systematic experiments regarding the influence of the binder composition upon the development of smoke or fumes have shown that in particular aromatic compounds constitute the primary cause for the disturbing development of smoke. All further experiments or tests therefore were directed towards producing highly-filled, but still castable insulation mixtures containing a pronounced aliphatic binder.

The fillers have the function of improving the insulating properties of the inhibitor coating. The proportion of filler is limited both by the workability of the mass employed for the insulating layer as well as also by the mechanical properties of the mixture.

It is known to use as the filler, inorganic substances possessing low thermal conductivity, for instance, asbestos, mica, and quartz in powder form.

Furthermore, there are used cooling agents, that is to say, solid inorganic or organic compounds, which at elevated temperatures markedly endothermically decompose into gaseous products, and thus, cool their surrounds.

For instance, there are used compounds containing water of crystallization, such as aluminium sulfate, aluminium fluoride, lithium metaborate, magnesium sulfate, sodium silicate or ammonium salts containing water of crystallization or free from water of crystallization, such as ammonium oxalate, ammonium sulfate, ammonium borate or compounds which easily decompose such as urea or melamine.

Due to the large proportion of cooling agent in the insulating layer it is possible to:

(a) improve the insulating properties,

(b) reduce the quantity of coarse carbonization products, which result from organic binders,

(c) reduce the formation of smoke,

(d) avoid clogging of the nozzles

Cooling agents are more suitable fillers than inert fillers, in that an insulating layer with improved insulating properties is achieved. The cooling agent should be present in a granulometric form of high packability, so that with good casting or pouring properties there is possible a high volumetric proportion of of filler.

When speaking in terms of the packability of a dispersed filler there is to be understood the proportion by volume of the pure filler with complete compaction by jarring or shaking. The packability P is the quotient of the shaking density ψ_R and the filler density ψ. This can be expresed by the following equation:

$$P = \frac{\psi_R}{\psi}$$

As the cooling agent aluminium hydroxide, Al $(OH)_3$, is particularly suitable, possessing a density equal to 2.41 g/cm^3 and a shaking

density equal to 1.500 to 1.545 g/cm³.

With such aluminium hydroxide, Al $(OH)_3$, thre can be realized still good castable insulating layers with a proportion of 50 to 70 parts by volume binder and 50 to 30 parts by volume cooling agent.

The binder is preferably composed of an isocyanate-containing polyether pre-adduct, a diamine hardener and an aliphatic plasticizer.

The pre-adduct preferably contains a molar mass of 2000—3000 grams/Mole, has an isocyanate content of 4—9 percent by weight and a viscosity of 300—700 centipoise at 100° C.

On the one hand, in order to be able to lower the viscosity of the pre-adduct to a degree required for the casting process, and, on the other hand, to reduce the aromatic proportion to such an extent that with slight formation of smoke there is still insured for satisfactory adhesion, there are undertaken the following measures:

(a) Complete reaction of the pre-adduct with an aromatic diamine and the addition of an aliphatic plasticizer.

Preferably, the pre-adduct for the binder is stochiometrically cross-linked with the aromatic diamine and 80—60 parts by weight of such pre-adduct cross-linked with the diamine is admixed with 20—40 parts by weight of the plasticizer. If desired, the aromatic diamine may be added in a dissolved state to the aliphatic plasticizer prior to mixing with the pre-adduct.

(b) Complete reaction of the pre-adduct with a stochiometric mixture of an aromatic diamine and a higher molecular triol, the pre-adduct for the binder being stochiometrically cross-linked with NH_2 and OH, the cross-linking agent containing 10—50 mol % NH_2 and 90—50 mol % OH. The aromatic diamine may be added in a dissolved state to the polyol.

Between the solid propellent charge and the insulating layer there is located a protective layer which initially must be applied to the propellent charge. For this protective layer there is preferably employed a completely moisture-hardened, low-molecular triisocyanate.

This protective layer has the following functions:

(a) To improve the adhesion of the insulating layer at the propellent charge owing to its high concentration of urea groups formed from free isocyanate and atmospheric moisture.

(b) To form a barrier against the migration of the plasticizer owing to its high degree of cross-linking due to the tri-functionality and the small molar or molecular mass.

This barrier functions in both directions in the event that both the insulating layer as well as also the propellent charge contains plasticizer. The second property is important since the plasticizer migration in the one or the other direction constitutes the cause of the impairment—which becomes increasingly more pronounced as a function of time—of the adhesion of the coating at the propellent charge until complete detachment of the coating from the propellent charge.

For this protective layer there is especially suitable the following triisocyanate:

triphenylmethane—4,4',4''-triisocyanate.

The lacquer-technological properties can be improved by the addition of additives, for instance 10 to 100 parts by weight of butyl acetate as the mean polar mean boiler to the 20%-packaged solution in methyl chloride of the aforementioned triisocyanate.

This improvement can be readily proven or ascertained by virtue of the good anchoring of the protective layer at the propellent charge and a good wetting, leading to a homogeneous film formation.

In order to transform the protective layer applied by spraying, coating or immersion into a defined condition, i.e. into a completely set or cured condition, within a useful period of time, the propellent charges provided with a protective layer are subjected to an evaporation time of approximately 1 to 24 hours and for at least 10 hours (preferably 15 hours) to a temperature of 60° C and a relative humidity of 70% to 90%. Consequently, the wetting process—which at room temperature and depending upon the humidity of the air lasts for 1 to 3 weeks—can be shortened.

(D) Description of Two Exemplary Embodiments of the Invention

The invention will be now described in greater detail in conjunction with two exemplary embodiments discussed hereinafter.

Example 1.

The propellent charge is initially coated with a protective- and adhesion layer. This layer consists of a solution of:

20 parts by weight triphenylmethane-4,4',4''-triisocyanate
80 parts by weight methylene chloride
30 parts by weight butyl acetate.

The solution must then be applied in a thin condition. After an evaporation time of 1 hour the protective layer is cured or hardened for 15 hours at 60° C in a moist atmosphere, preferably in an air circulating oven or furnace with closed air valves and with a vessel filled with water located in the oven compartment or chamber.

Thereafter there is applied an insulating layer. This consists of a mixture containing:

223.6 grams of a polyether-pre-adduct possessing an isocyanate content of 4.3% as hardener.
156 grams acetyltri-n-butyl-citrate.

This mixture is degasified and dewatered in a kneader for half an hour at 70° C and a pressure of about 1 mm Hg pressure (Torr).

Thereafter there is added to the mixture the following:

780 grams of aluminium hydroxide as the cooling agent.
Granulation size $< 150\ \mu$.
Packability 62%.

This mixture is then admixed or stirred in the kneader for half an hour under the same conditions.

Thereafter there is added to the mixture the following:

40.4 grams molten 4,4'-methylene-bis-(2-chloroaniline) as the hardener.

The new mixture is again processed for 5 minutes in the kneader and subsequently applied to the propellent charge. For this purpose the propellent charge is placed into a casting mold, so that there is formed a 2 mm thick hollow space between the casting mold and propellent charge into which there is poured the aforementioned mixture. The propellent charge consists of a 2-basic powder and possesses a diameter of 100 mm. The inner surface of the casting mold is provided with a "TEFLON" coating ("TEFLON" is a registered Trade Mark). After curing or hardening for 10 hours at 60° C the propellent charge provided with the coating can be removed from the casting mold. The curing or hardening temperature may be in the range of 20° C to 80° C.

After undergoing temperature-alternating tests of 6 cycles at $-50°$ C to $+60°$ C such processed propellent charge displayed no changes in the adhesion of the coating.

Stand burn-off in test chambers with nozzles of large flow constriction took place without disturbances both with tested as well as untested propellent charges at extreme temperatures of $-40°$ C and $+60°$ C.

Smoke measurements produced results in the order of less than 8dB.

Example 2.

The protective layer is the same as that described with respect to the first exemplary embodiment of Example 1.

Thereafter there is applied the insulating layer. This consists of a mixture containing the following:

364.2 grams of a polyether-pre-adduct possessing an isocyanate content of 6.5%.
780.0 grams aluminium hydroxide.
155.8 grams of a hardener solution consisting of 22.4 grams 4,4'-methylene-bis-(2-chloroaniline),
133.4 grams castor oil possessing an hydroxide content of 5%.

Initially the pre-adduct is degasified and dewatered in a kneader at a temperature of 70° C and a pressure of 1 mm Hg pressure (Torr), and thereafter there is added the hardener solution. After stirring or mixing for 5 minutes the mixture is filled into the mold under the same conditions as discussed above in conjunction with the first embodiment of Example 1.

Propellent charges provided with such coating gave the same results during all tests.

The inhibitor coatings can be composed of the following components.

1. *Filler-Cooling Agent*
Aluminium hydroxide possessing a packability of 64%.

2. *Binder*
PU (A) Polyurethane—partially aliphatic—pre-adduct containing 4.3% content of isocyanate which is stoichiometrically cross-linked with 4,4'-methylene-bis-(2-chloroaniline).

PU (B) Polyurethane—partially aliphatic—pre-adduct containing 6.5 % content of isocyanate which is stoichiometrically cross-linked with 30 Mol % NH_2 from 4,4'-methylene-bis-(2-chloroaniline)
70 Mol % OH from castor oil with 5% OH.

PU (C) Polyurethane—purely aliphatic—produced in a one-shot process from polyoxypropyleneglycol and trimethylolpropane cross-linked with 4,4'-methylene-bis-(cyclohexylisocyanate) catalized with
0.5% stannous dibutyl-dilaurate
0.5% iron acetyl-acetonate

Composition of the mixture in Mol % of the reactive groups of the participating partners

Diol 70
Triol 30
CNO 100

PE Soft foam unsaturated polyester hardened by the addition of methyl ethyl-ketone peroxide and cobalt naphthanate.

WM Acetytri-n-butyl citrate.

DPA Diphenylamine (an aromatic substance which is readily soluble in polyurethane and added for comparative purposes).

DA 4,4'-methylene-bis-(2-chloroaniline).

TABLE I

Influence of the Proportion of Cooling Agent Upon the Development of Smoke

Ex.	Cooling Agent	Binder PE	PU (A)	PU (B)	PU (C)	WM	DPA	Aromatic Proportion	(1) Smoke
4	60		40						7.0
3	45		55						10.5

TABLE II

Influence of the Binder Composition Upon Smoke Development

Ex.	Cooling Agent	Binder PE	PU (A)	PU (B)	PU (C)	WM	Aromatic Proportion DPA	DA	(1) Smoke
1	60	40						11	15
2	45		53.5				1.5	11	13.5
3	45		55.0					11	10.5
4	60		40.0					11	7.0
5	60		28.0			12.0		7.8	6.0
6	60			40				4.3	6.0
7	60				40			0	4.3

(1) The smoke measurement is given in dB, with average or mean weakening of the light during the burning-off.

Finally it is to be mentioned that all of the concentrations given herein, unless otherwise stated, are in percent by weight.

WHAT WE CLAIM IS:—

1. A solid rocket propellant charge protected against undesired burning off by an inhibiting coating comprising a protective and adhesion layer and a castable insulating layer for protecting said propellant charge against undesired burning off, said protective and adhesion layer being located between the insulating layer and the propellant charge and consisting of a completely hardened polyisocyanate forming a barrier against plasticiser migration, said castable insulating layer containing a binder and a filler, the binder consisting of a castable mass which has low smoke developing properties in order to avoid clogging of the rocket nozzles and reduced visibility, the filler consisting of a cooling agent which is composed of a granular material having a grain size less than 150 microns, and the grain size is adjusted such that there is attained a packability of at least 55 percent by volume, the packability being designated by the symbol P which is the quotient of the solid density ψ in grams/cm^3 and the shaking density ψ_R in grams/cm^3, wherein:

$$P = \frac{\psi_R}{\psi}$$

2. A solid rocket propellant charge according to Claim 1, wherein said cooling agent comprises aluminium hydroxide.

3. A solid rocket propellant charge according to Claim 1 or 2, wherein the insulating layer contains 50 to 70 parts by volume binder and 50 to 30 parts by volume cooling agent.

4. A solid rocket propellant charge according to any of the preceding Claims, wherein a pre-adduct for the binder contains a molar mass of 2000 to 3000 grams/Mole, an isocyanate content of 5 to 9 percent by weight and a viscosity of 300 to 700 centipoise at 100° C.

5. A solid rocket propellant charge according to Claim 4, wherein the pre-adduct for the binder is stoichiometrically cross-linked with an aromatic diamine, and wherein 80 to 60 parts by weight of such pre-adduct cross-linked with the diamine is admixed with 20 to 40 parts by weight of a plasticizer.

6. A solid rocket propellant charge accord-

TABLE I

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2	45		53.5				1.5	11	13.5
3	45		55.0					11	10.5
4	60		40.0					11	7.0
5	60		28.0			12.0		7.8	6.0
6	60			40				4.3	6.0
7	60				40			0	4.3

(1) The smoke measurement is given in dB, with average or mean weakening of the light during the burning-off.

Finally it is to be mentioned that all of the concentrations given herein, unless otherwise stated, are in percent by weight.

WHAT WE CLAIM IS:—

1. A solid rocket propellant charge protected against undesired burning off by an inhibiting coating comprising a protective and adhesion layer and a castable insulating layer for protecting said propellant charge against undesired burning off, said protective and adhesion layer being located between the insulating layer and the propellant charge and consisting of a completely hardened polyisocyanate forming a barrier against plasticiser migration, said castable insulating layer containing a binder and a filler, the binder consisting of a castable mass which has low smoke developing properties in order to avoid clogging of the rocket nozzles and reduced visibility, the filler consisting of a cooling agent which is composed of a granular material having a grain size less than 150 microns, and the grain size is adjusted such that there is attained a packability of at least 55 percent by volume, the packability being designated by the symbol P which is the quotient of the solid density ψ in grams/cm^3 and the shaking density ψ_R in grams/cm^3, wherein:

$$P = \frac{\psi_R}{\psi}$$

2. A solid rocket propellant charge according to Claim 1, wherein said cooling agent comprises aluminium hydroxide.

3. A solid rocket propellant charge according to Claim 1 or 2, wherein the insulating layer contains 50 to 70 parts by volume binder and 50 to 30 parts by volume cooling agent.

4. A solid rocket propellant charge according to any of the preceding Claims, wherein a pre-adduct for the binder contains a molar mass of 2000 to 3000 grams/Mole, an isocyanate content of 5 to 9 percent by weight and a viscosity of 300 to 700 centipoise at 100° C.

5. A solid rocket propellant charge according to Claim 4, wherein the pre-adduct for the binder is stoichiometrically cross-linked with an aromatic diamine, and wherein 80 to 60 parts by weight of such pre-adduct cross-linked with the diamine is admixed with 20 to 40 parts by weight of a plasticizer.

6. A solid rocket propellant charge accord-

ing to Claims 4 or 5 wherein the pre-adduct for the binder is stoichiometrically cross-linked with NH_2 and OH, and the cross-linking agent contains 10 to 50 Mol % NH_2 and 90—50 Mol % OH.

7. A solid rocket propellant charge according to Claim 5, wherein the aromatic diamine is 4,4' - methylene - bis - (2 - chloroaniline).

8. A solid rocket propellant charge according to Claim 5, wherein the plasticizer is an aliphatic plasticizer, said aliphatic plasticizer being acetytri-n-butyl citrate.

9. A solid rocket propellant charge according to Claim 6, wherein the OH-radical is derived from castor oil.

10. A method of producing a solid rocket propellant charge protected against undesired burning-off by an inhibiting coating as Claimed in Claim 1 wherein said method includes preparing the insulating layer by admixing, in a kneader, a pre-adduct, a cooling agent, and an aromatic diamine, and either an aliphatic plasticizer or an aliphatic polyol, mixing being continued until the pre-adduct and diamine have completely reacted.

11. The method according to Claim 10, wherein the insulating layer of the inhibitor coating is applied to the propellent charge by casting, said insulating layer being hardened at a temperature in the order of 20° C to 80° C.

12. The method according to Claim 11, wherein prior to casting the insulating layer there is applied a protective- and adhesion layer composed of 20 parts by weight triphenylmethane-4,4',4''-triisocyanate, 80 parts by weight methylene chloride, and 10 to 100 parts by weight of a mean polar mean boiler.

13. The method according to Claim 12, wherein the protective- and adhesion layer, prior to casting of the insulating layer is completely hardened after an evaporation time of approximately 1 to 24 hours and for at least 10 hours at a temperature of about 60° C and a relative air moisture content in the order of 70% to 90%.

14. The method according to Claim 13, wherein the aromatic diamine is added in a dissolved state to the aliphatic plasticizer.

15. The method according to Claim 13, wherein the aromatic diamine is added in a dissolved state to the aliphatic polyol.

16. A solid rocket propellant charge protected against burning off by an inhibiting coating substantially as herein described.

17. The method of producing a solid rocket propellant charge protected against burning off by an inhibiting coating substantially as herein described.

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