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COMBUSTION INHIBITOR FOR GAS-PRODUCING CHARGES

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This invention relates to gas-producing charges having surfaces which are inhibited or restricted from burning and to plastic inhibitor compositions for this purpose.

In the contemporary development of solid propellants, it has been found necessary to the attainment of desirable characteristics to inhibit some surfaces of the combustible gas-producing charges from burning. Up to the present time the most desirable inhibitor has been found to be cellulose acetate. Cellulose acetate has been applied to grains of gas-producing compositions and in particular to rocket grains of double-base smokeless powder in many ways. Initially the grains were inhibited by cementing plastic patches to the surface or applying a convolute wrapping of cellulose acetate sheet material suitably moistened with an adhesion promoting agent such as acetone or by suitable adhesive composition. As the art developed, the inhibitor structures were preformed and, in accordance with one procedure, the gas-producing charge is cast directly into preformed cylindrical cellulose acetate tubes. In accordance with alternative methods, the charge is initially prepared by casting or extrusion and then fitted into a hollow cylinder of cellulose acetate which had been prepared by wrapping or extrusion. Restriction of end surfaces has usually been achieved by bonding preformed plates to the desired portions of the grain ends.

The cellulose acetate inhibitor and inhibitors made of similar materials such as ethyl cellulose have been reasonably satisfactory and have contributed greatly to the development of improved gas-producing charges. However, it has been recognized for several years that even the preferred cellulose acetate restriction left much to be desired. Probably one of the most serious faults of cellulose acetate is found in the fact that when the usual double-base smokeless powder grain is restricted with this plastic material, an undesirably large amount of nitroglycerin migrates from the powder grain into the inhibitor during storage. Of probably equal seriousness is the migration of plasticizer from the inhibitor layer into the base grains. Ballistically the two effects are additive, since loss of nitroglycerin from the grain and pick-up of cooling plasticizer by the grain lower the overall potential. This problem has not been a serious one where the powder grains were employed immediately or where the time of storage was short. However, it is evident that for military uses in particular, it is usually necessary to stockpile large numbers of such gas-producing grains under varying conditions of storage for long periods of time. For accuracy and optimum performance it is essential that the grains perform in substantially the same manner at the end of a storage period as at the beginning of the storage period. Depending upon the amount of nitroglycerin migration into the inhibitor, the characteristics of the grain necessarily change during storage. Due to the leaching of the nitroglycerin from the peripheral surface of the grain, the ballistics of the charge are changed and the grain structure itself becomes characterized by

different structural strengths and ignition characteristics depending upon the nitroglycerin content at a particular point. Furthermore, burning time is seriously affected by plasticizer migration. It is apparent that where the gas-producing charge is employed as the sole means of propulsion of a guided missile such variations in the make-up and structural characteristics of the burning charge can have serious ramifications with respect to accuracy and overall performance.

With respect to the inhibitor itself, it has been found that the initial migration of the nitroglycerin into the cellulose acetate has actually improved the initial bond between the grain and restriction. However, as the amount of nitroglycerin builds up in the inhibitor, the plastic becomes progressively softer and the inhibitor actually fails when sufficient of the nitroglycerin has been absorbed. The life of a cellulose acetate inhibitor surface can be prolonged by increasing the thickness of the restriction. However, it is apparent that, although the art has been forced to thicker inhibitors, this is an undesirable approach to the problem, since for the same size rocket motor and a given propellant composition any increase in the thickness of the inhibitor layer must necessarily work a proportional decrease in the amount of gas-producing pay load.

In view of these recognized faults of even the preferred cellulose acetate inhibitor, there has been a continuous effort on the part of the explosives art to develop a material for use as a restriction which will give the necessary bond between the inhibitor and the gas-producing charge, which will not absorb nitroglycerin or other explosive plasticizer in any substantial amount, and which will retain the necessary bonded relationship for the necessary period of time even though subjected to varying storage conditions in terms of temperature changes and the like. This effort on the part of the art has been completely unsuccessful, however, and at the present time cellulose acetate, despite its known faults, is still considered to be the best available combustion inhibitor for most gas-producing charges.

Now in accordance with the present invention, plastic compositions may be prepared and gas-producing charges may be fabricated employing such plastic compositions which are characterized by greatly improved properties. The compositions of the invention will form excellent bonds with gas-producing charges, particularly those containing nitrocellulose, without detrimental migration of explosive plasticizer from the gas-producing grain.

Generally described, the present invention is a gas-producing charge comprising a body of combustible gas-producing composition having at least part of its surface covered by a burning inhibitor layer of plastic composition bonded thereto, said plastic composition comprising the cured product of a mixture containing from 25 to 50% monomeric butyl methacrylate, from 25 to 45% of a finely-divided copolymer of vinyl chloride with not more than about 5% of vinyl acetate, from 5 to 30% of finely-divided polymeric methyl methacrylate, and 5 to 20% of a nonvolatile plasticizer for the vinyl chloride-vinyl acetate copolymer. The gas-producing charge is preferably a smokeless powder composition and may be a single base formulation comprising nitrocellulose, but will ordinarily be a double-base composition containing nitrocellulose and nitroglycerin or similar explosive plasticizer such as other liquid explosive nitric esters. The gas-producing charge may also be formed from other combustible materials currently employed by the art such as ammonium nitrate and nitroguanidine which may be compacted into suitable physical form with or without the use of a binding agent or matrix such as nitrocellulose or various synthetic resins. The gas-producing charge

may have any desired configuration but in accordance with current practice is normally a cylindrical grain having its outer cylindrical surface inhibited from burning in accordance with the invention. An inhibitor layer may also be employed on either or both ends of the grain depending upon the internal geometry of the grain. In some embodiments, such as in perforated grains, it is desirable to inhibit the outer surface and perforation surface and allow only end burning.

Also included in the invention are the cured and uncured inhibitor compositions comprising from 25 to 50% monomeric butyl methacrylate, from 25 to 45% of a copolymer of vinyl chloride with not more than about 5% of vinyl acetate, from 5 to 30% of polymeric methyl methacrylate, and 5 to 20% of a nonvolatile plasticizer for the vinyl chloride-vinyl acetate copolymer. In accordance with the invention and in order to obtain even stronger bonds which will survive repeated cycling from low to high temperature in storage, amounts up to and including 15% of a bifunctional cross-linking monomer may also be included in the composition. The most desirable bifunctional cross-linking monomer is the dimethacrylate of polyethylene glycol 200 (BCM). Improved results have also been obtained with divinyl benzene, although some bond failures after extended storage at 66% C. have still been encountered. With BCM, on the other hand, excellent results are still obtained at such temperatures.

As will be illustrated in the subsequently presented examples, it has been found that the ranges of incorporation for the various constituents of the plastic inhibiting material of this invention are critical to obtaining a satisfactory inhibitor, particularly when the inhibitor is employed to restrict from burning surfaces of the usually employed smokeless powder charges comprising nitrocellulose and nitroglycerin.

The use of less than 25 parts of butyl methacrylate normally results in bond failure during storage, while the use of more than 50 parts of butyl methacrylate monomer results in a mixture which allows the polymeric constituents of the composition, and particularly the polymethyl methacrylate, to settle out prior to curing. Furthermore, when a composition containing more than 50 parts of butyl methacrylate monomer is employed, the resulting cured product becomes brittle with resulting bond failure and cracking of the restriction during curing, storage, and temperature cycling.

If less than 25 parts of polyvinyl chloride-acetate copolymer is employed, bond failure normally results and nitroglycerin is absorbed from a double-base gas-producing charge of smokeless powder. On the other hand, if more than 45 parts of the copolymer are employed, the uncured mix rapidly becomes too viscous to handle satisfactorily and also prevents the formation of even a satisfactory initial powder-inhibitor bond. In addition, the increased viscosity makes it prohibitively difficult to remove entrapped air from the uncured composition. Furthermore, it has been found that if the copolymer contains more than about 5% vinyl acetate, either the composition does not set up at all or else the bond fails even at room temperature storage due to the softness of the composition.

The presence of at least 5% polymethyl methacrylate is essential to the formation of a satisfactory bond. However, if more than 30% of polymethyl methacrylate is employed, bond failures are again obtained during storage.

The presence of at least 5% of a plasticizer for the vinyl chloride-vinyl acetate copolymer is essential to a composition which does not become so brittle upon curing that the bond between the powder grain and the inhibitor is destroyed. However, if more than 20 parts of plasticizer is employed, the resistance of the inhibitor to nitroglycerin absorption is again lowered and failure of the inhibitor itself is usually obtained in storage.

The incorporation of the bifunctional cross-linking monomer is optional depending upon the use to which the restricted gas-producing charges are to be put. It is preferred, however, that the cross-linking agent be employed in all compositions since its presence has been found to preserve the integrity of the bond between the gas-producing charge and the inhibitor under all temperature conditions which can reasonably be expected even during military operations. The cross-linking obtained by the incorporation of the cross-linking agent does cause a hardening of the inhibitor. However, the amount of hardening obtained is not disadvantageous as long as not more than 15 parts of the cross-linking agent is employed. When more than 15 parts is employed, undesirable brittleness of the cured product is obtained with resulting bond faliures.

The inhibitor compositions in accordance with the invention cure rapidly with conventional polymerization catalysts for acrylic compounds and at low temperatures. Cure time depends on the thickness of the restriction layer and the type and amount of catalyst.

Having generally described the invention, the following examples are given in order to illustrate operable compositions and gas-producing charges and to illustrate the criticality of the proportions of the plastic inhibitor composition of the invention.

In Table 1, Examples 1–31 are included to demonstrate operable inhibitor compositions and to illustrate the necessity of observing the limitations above set forth. Each of the compositions set forth was applied to a cylindrical grain of double-base smokeless powder containing nitroglycerin by concentrically disposing the powder grain in an oversized cylindrical mold equipped with a steam jacket and filling the resulting annulus between grain and mold with the uncured mix. The composition was cured for about one hour at a temperature of 80° C. After removal from the mold, the restriction and bond were examined. The inhibited grains were then placed in hot storage and unless otherwise indicated, were maintained at about 60° C. for a period of three weeks and examined at weekly intervals. The observations made are set forth in Table 1 under "Remarks." All the compositions in Table 1 contained about 4% of Luperco ATC (a 50:50 mixture of benzoyl peroxide and tricresyl phosphate) as a polymerization catalyst.

TABLE 1

Example No.	BMA	PVC–A	PMMA	Plasticizer	Percent Cross-linking Agent	Remarks
1	40	30	20	10		good bond—good plastic.
2	14.9	33.1	18.9	33.1		bond failed in hot storage—plastic softened.
3	35	30	20	15		good bond—good plastic.
4	26.2	34.5	19.6	19.6		satisfactory bond—plastic satisfactory but softened somewhat after hot storage.
5	26.1	28.6	28.6	16.7		Do.
6	38	28.5	18.5	15		good bond—good plastic.
7	35	25	25	15		good bond—good plastic—uncured mix thin with slight settling out of PMMA.
8	15	35	25	25		bond failed in hot storage—plastic softened.
9	20	40	20	20		Do.
10	47	25	30	8		good bond—plastic satisfactory but somewhat brittle.
11	50	37.5		12.5		bond failed in hot storage—plastic cracked.

TABLE 1.—Continued

Example No.	BMA	PVC-A	PMMA	Plasticizer	Percent Cross-linking Agent	Remarks
12	25	30	20	25 (15% DAP) (10% TCP).		bond good (in hot storage the plastic softened undesirably).
13	35	30	20	15		good bond—good plastic.
14	25	30	20	15	10 BCM	satisfactory bond—plastic satisfactory but softened somewhat in hot storage.
15	30	30	20	20		good bond—plastic satisfactory but exhibited slight softening in hot storage.
16	25	30	20	25		bond failed in hot storage—plastic softened.
17	30	30	20	20		satisfactory bond—plastic satisfactory but softened slightly.
18	20	30	20	15	15 BCM	bond failed in hot storage—plastic satisfactory.
19	50	30	10	5	5 BCM	satisfactory bond—plastic satisfactory but becoming brittle—uncured mix thin and some PMMA settled out while standing.
20	30	20	25	15	10 BCM	bond failed in hot storage—plastic satisfactory —uncured mix was very thin allowing the PMMA to settle out.
21	40	40	10	5	5 BCM	good bond—good plastic.
22	40	45	5	5	5 BCM	satisfactory bond—satisfactory plastic—uncured mix viscous and difficult to handle.
23	40	30	5	15	10 BCM	satisfactory bond—plastic satisfactory but showed some softening in storage.
24	30	35	15	5	15 BCM	satisfactory bond—satisfactory plastic—uncured mix viscous and difficult to handle.
25	25	30	15	10	20 BCM	bond failed—plastic very brittle and cracked.
26	40	30	15	10 TCP	5 BCM	good bond—good plastic—excellent temperature properties.
27	35	30	20	10 TCP	5 DVB (18%)	good initial bond—good plastic—bond failed after extended storage at 66° C.
28	30	30	20	10 TCP	10 DVB (18%)	good initial bond—plastic satisfactory although somewhat brittle.
29	30	30	20	10 TCP	10 DVB (45%)	good bond—good plastic.
30	40	30	20	5 TCP	5 DVB (45%)	good initial bond—good plastic—bond failed after extended storage at 66° C.
31	30	30	20	10 TCP	10 BCM	good bond—good plastic—excellent temperature properties.

BMA—n-butyl methacrylate monomer.
PVC-A—polyvinyl chloride-acetate copolymer.
PMMA—polymethyl methacrylate.
BCM—dimethacrylate of polyethylene glycol 200.
DVB—divinylbenzene.
TCP—tricresyl phosphate.
DAP—diallyl phthalate.

In Table 2, Examples 32–37 are presented to illustrate the criticality of the 95/5 ratio of PVC/PVA. Thirty (30) percent of the PVC–PVA copolymer was employed in all cases. The commercial designation of the polymer employed is set forth in parenthesis. The inhibitor was applied to double-base smokeless powder grains by the casting process employed in Examples 1–31. Observations are given under "Remarks."

TABLE 2

Example No.	BMA	PMMA	PL	PVC/PVA	Catalyst*	Remarks
32	40	20	10 TCP	95/5 (VYNV—1)	4	excellent for all uses except extended hot storage.
33	40	20	10 TCP	85-88/12-15 (VYHH)	4	very thick, very tacky, air bubbles—no casting.
34	40	20	10 TCP	100/—(QYNV)	4	Bond failed—becomes very soft in hot storage.
35	40	20	10 TCP	88.5-91.5/8.5-11.5 (VYNS-3).	4	very thick—air bubbles—no casting.
36	40	20	10 TCP	100/—(Geon 121)	4	bond failure.
37	40	20	10 8HP	100/—(Geon 121)	4	Do.

BMA—n-butyl methacrylate monomer.
PMMA—polymethyl methacrylate.
PL—plasticizer.
PVC/PVA—polyvinyl chloride/acetate copolymer.
TCP—tricresyl phosphate.
8HP—di-2-ethylhexyl tetrahydrophthalate.
*Catalyst—Luperco ATC (50/50 benzoyl peroxide) tricresyl phosphate.

Even when the amount of PVA in the copolymer is 5% or less, difficulty is sometimes encountered in obtaining a casting if the particle size of the copolymer is unduly large. The copolymers which are commercially produced for plastisols and organosols and contain less than 5% of PVA are generally satisfactory as furnished. Any difficulty encountered can be overcome by allowing more time for the copolymer to go into solution or by ball-milling the PVC–A to reduce particle size before use.

Example 38

Four groups of solid, cylindrical, end-burning grains were prepared. The outer surfaces of group 1 were conventionally restricted with cellulose acetate, while the outer surfaces of the remaining groups were restricted in accordance with the invention. The outer surfaces of group 2 were restricted by casting around the grains a mix containing 40% monomeric butyl methacrylate, 30% polyvinyl chloride-acetate copolymer, 20% polymethyl methacrylate, and 10% of tricresyl phosphate. Two percent of benzoyl peroxide based on the weight of butyl methacrylate monomer was employed as polymerization catalyst. Groups 3 and 4 were restricted by composition similar to that of group 2 except that 5% BCM was substituted for 5% of the butyl methacrylate in group 3 and 10% of BCM was substituted for 10% of the butyl methacrylate in group 4. The restrictions of groups 2, 3 and 4 were all cured at 100° C. for one hour.

All four groups of restricted grains were placed in 60° C. storage for 36 weeks and at the end of each week a grain from each group was removed and its restriction analyzed to determine nitroglycerin absorption. In the analysis the standard $TiCl_3$ method on a methylene chloride extract was employed. At the end of 12 weeks the cellulose acetate restriction contained 29% by weight of nitroglycerin. At the end of 12 weeks it was noted

that nitroglycerin absorption had practically leveled off in all the restrictions. At the end of 36 weeks, the restrictions of groups 2, 3, and 4 contained a maximum of 10%, 8%, and 7.5%, respectively.

Example 39

Restricted grains similar to those of groups 2, 3, and 4 were placed in 80° C. storage for 9 weeks. Bond failures occured in group 2 at the end of two days. At the end of 9 weeks plastic and bonds in groups 3 and 4 were excellent. Maximum absorption of nitroglycerin in group 3 was 10.7% and in group 4 was 9.8%.

The plastic inhibitor compositions of the invention may be applied to external or perforation surfaces of gas-producing charges in any desired manner. The preferred method is to place an unrestricted grain into an oversized mold and then introduce the curable mix or slurry into the annulus around the grain in such a manner as to prevent entrapment of air. This is best accomplished by introducing the mix under pressure into the base of the mold. The entire mold is then subjected to curing conditions until the plastic has set and a bond has been formed. Perforation surfaces may be similarly inhibited by employing undersized forms and then introducing the uncured mix into the space between form and perforation surface. Alternatively, the plastic inhibitor may be initially molded and the propellant grain subsequently cast in the hollow inhibitor cylinder, thus using this cylinder as a mold or casting container. A satisfactory bond is obtained between inhibitor and grain during the curing of the grain. In other instances it may be desired to apply the composition by crosshead extrusion techniques. Another operable method, although not as desirable, is to separately prefabricate both the inhibitor and the grain to close tolerances, apply a mutual solvent to the surface of the grain, and then slide the grain into the inhibitor cylinder.

It is especially preferred, however, to cast the inhibitor around the finished grain or in a perforation, since it is by this procedure that the best bond is obtained. The enhanced bond thus produced results from the solvent action of the monomeric butyl methacrylate monomer on the nitrocellulose on the surface of the gas-producing grain. Since the butyl methacrylate is also a solvent for the polymeric constituents of the inhibitor, the nitrocellulose polymer and the polyvinyl chloride acetate-polymethyl methacrylate of the inhibitor are held in mutual solution at the surface of the grain. Thus, when the butyl methacrylate is polymerized, a strong bond is obtained. The strength of this bond and the ruggedness of the inhibitor composition as a whole is further enhanced by cross-linking of the butyl methacrylate when the bifunctional cross-linking monomer such as BCM or divinylbenzene is employed.

It has been found that any of the conventional plasticizers for PVC–A employed by the art are operable when employed in the critical amount. Of all of those employed, however, tricresyl phosphate is preferred in view of its plasticizing properties and further in view of its fireproofing effect on the composition. Other plasticizers which may be employed include, without limitation, diallyl phthalate, trioctyl phthalate, trioctyl phosphate, dibutyl sebacate, and dibutyl adipate.

A variety of polymerization catalysts for acrylic monomers are known to the art and may be employed in place of any of the catalysts illustrated by the examples. Such materials include lauroyl peroxide, di-tert-butyl peroxide, tertiary butyl hydroperoxide, cumene hydroperoxide, methyl ethyl ketone peroxide, and tertiary butyl perbenzoate. Of all of the operable catalysts those of the peroxide type are the most desirable. Benzoyl peroxide is especially preferred in view of the low temperature necessary to effect polymerization with this material.

In some applications it may be desired to incorporate a filler material in the restriction composition such as glass wool, asbestos floc, and the like.

Since modifications of the invention will be apparent to the art, the invention is limited only by the scope of the appended claims.

What we claim and desire to protect by Letters Patent is:

1. A curable mixture adapted for inhibitor application to combustible gas-producing charges comprising by weight from 25 to 50% monomeric butyl methacrylate, from 25 to 45% of a copolymer of vinyl chloride with not more than about 5% of vinyl acetate, from 5 to 30% of polymeric methyl methacrylate, and from 5 to 20% of a nonvolatile plasticizer for the vinyl chloride-vinyl acetate copolymer.

2. A mixture according to claim 1 containing a polymerization catalyst for monomeric butyl methacrylate.

3. A mixture according to claim 1 in which the plasticizer is tricresyl phosphate.

4. A curable mixture adapted for inhibitor application to combustible gas-producing charges comprising by weight from 25 to 50% monomeric butyl methacrylate, from 25 to 45% of a copolymer of vinyl chloride with not more than about 5% of vinyl acetate, from 5 to 30% of polymeric methyl methacrylate, an amount not exceeding 15% of the dimethacrylate of ethylene glycol, and from 5 to 20% of a nonvolatile plasticizer for the vinyl chloride-vinyl acetate copolymer.

5. A mixture according to claim 4 containing a polymerization catalyst for monomeric butyl methacrylate.

6. A mixture according to claim 4 in which the plasticizer is tricresyl phosphate.

7. A composition of matter comprising the cured product of a mixture containing from 25 to 50% monomeric butyl methacrylate, from 25 to 45% of a copolymer of vinyl chloride with not more than about 5% of vinyl acetate, from 5 to 30% of polymeric methyl methacrylate, and from 5 to 20% of a nonvolatile plasticizer for the vinyl chloride-vinyl acetate copolymer, said product being adapted for inhibitor application to a combustible gas-producing charge.

8. A composition according to claim 7 in which the plasticizer is tricresyl phosphate.

9. A composition of matter comprising the cured product of a mixture containing from 25 to 50% monomeric butyl methacrylate, from 25 to 45% of a copolymer of vinyl chloride with not more than about 5% of vinyl acetate, from 5 to 30% of polymeric methyl methacrylate, an amount not exceeding 15% of the dimethacrylate of ethylene glycol, and from 5 to 20% of a nonvolatile plasticizer for the vinyl chloride-vinyl acetate copolymer, said product being adapted for inhibitor application to a combustible gas-producing charge.

10. A composition according to claim 9 in which the plasticizer is tricresyl phosphate.

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