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PROPELLANT COMPOSITION

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(Granted under Title 35, U.S. Code (1952), sec. 266)

The invention described herein may be manufactured and used by or for the Government for governmental purposes without the payment to us of any royalty thereon.

The present invention relates to combustible casing material and to the methods of making the same. More particularly the invention is concerned with combustible casing material that may be formed in the shape of, and serve as, combustible cartridge cases or the like.

The advantages of combustible cartridge cases will be apparent to those skilled in the art. The firing rates of weapons in which combustible cartridge cases are used may be increased substantially due to the elimination of the ejection operation which would also result in a saving of weight and space in the weapon. The problem of disposal of metal shell cases is eliminated, creating thereby a saving of metals which might become critically short in supply during times of emergency. Furthermore, the elimination of the conventional metal case results in a considerable saving in weight. An additional advantage of combustible cartridge cases may involve the possible reduction in gun erosion. Yet another use of combustible casing material would be in the manufacture of rocket casing that would be consumed as the rocket fuel was burned, thus eliminating a considerable dead weight found in prior metal rocket casings.

Prior methods and materials used for the manufacture of combustible casings have had the disadvantage that it has been difficult to maintain the stability, strength and ballistic properties of the combustible material. This is particularly true where non-crystalline thermoplastic material was used, since these materials undergo an extensive amount of "creep" under normal storage conditions. This "creep" is a "cold-flow" process which is proportional to temperature and applied load. These non-crystalline thermoplastic materials have proven unsuccessful as combustible casing material since they will quite readily deform under their own weight.

Another disadvantage of the prior art material is that the combustible casing material has added no appreciable propelling effect to the shell thus in no way allowing for the reduction in the propellant loading. Yet another disadvantage of the prior art is that known combustible casings are formed of laminations and thus are not readily adaptable to cheap and fast mass production as by, for example, molding.

Accordingly, a primary object of the present invention is the provision of a combustible cartridge case having the necessary strength characteristics and which will burn completely when fired in conventional weapons.

Another object of this invention is to provide a combustible casing constructed of propellant grains bonded together with a binder, thus allowing a reduction in the propellant loading.

Yet another object of this invention is to provide a composition of matter which may be molded into any desired shape and which will be smokeless when burned.

Other objects and advantages of the present invention

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will become apparent to those skilled in the art from a study of the accompanying disclosure.

In one of its broad aspects, the method of making the present invention consists of mixing one or more granulations and formulations of propellant grains with a resin binder so that the grains are held in a matrix of the resin. The quantity and size of the propellant grains which are held suspended in the resin matrix may be varied to give a uniformly porous structure to the combustible casing material. By using this method, a combustible material can be obtained which, as further pointed out below, leads to the feature of a mass burning rate which is to only a small extent dependent on structure or wall thickness. As previously indicated, the material may be formed into any desired shape or casing form by, for example, being molded in the shape of cartridge casings or rocket tubes which may then be filled with an appropriate propellant material.

The combustible casing material of the present invention should not be confused with prior combustible materials of the cast propellant type. In cast propellants, very careful attention is given to getting a propellant completely free of voids or porous structure and as homogeneous as possible in composition. Since cast propellants do not have a void or porous structure, it has a burning rate which is essentially dependent on the chemical composition. Thus, the mass burning rates of cast propellants, for a given grain size or web, are considerably lower than for the type of propellant composition disclosed in the present invention. Since cast propellants have a mass burning rate that is relatively low, there is a practical limitation on the size or thickness of a casing wall that may be constructed of the cast propellants. However, because of the burning properties of the propellant composition described herein, which are brought about by the introduction of controlled voids in the porous structure of the propellant material, and the size of the propellant grains suspended in the resin matrix it is ideally suited for applications where a heavy wall for structural strength and a short burning time is required.

The resin or binder materials which may be used by the process of this invention may be chosen from the large group of binding substances including polyesters, polyurethane and epoxy resins. Petrin acrylate which is a nitropolymer may also be used as a binder. The petrin acrylate monomer is a solid which is fused, mixed with the propellant grains and then cured at an elevated temperature. There are also other nitropolymers which are known to be suitable for binder material.

A number of granulations and formulations of propellant grains may be used with the binder material to form a combustible casing having controlled voids. The compositions of propellant grains which may be used are given below. Various other propellant agents may be used with the resin, as the only limitation on the propellants that may be used appears to be that they must be solids and chemically compatible with the resin used.

The resins and propellant grains are mixed in a mixer of the type which will avoid crushing of the propellant grains since any crushing would result in a mixture whose ballistics would be unpredictable and, therefore undesirable. One mixer which has been found suitable for use in the present invention is the Sigma blade type. A Sigma blade mixer consists of a container in which two arms, approximately in the shape of the letter Z, rotate in opposite directions to impart a kneading action to the material being mixed. However, the mixing operation

of the present invention is not limited to the use of the Sigma blade mixer but any mixer which will not crush the propellant grains would be suitable.

In some cases it has been found desirable to add fibers of various types, both natural and synthetic, such as, for example, nitrocellulose or cotton to the resin and propellant mixture. These various fibers give additional strength to the casing where such is necessary.

In order to point out more fully the nature of the present invention, the following specific examples are given of illustrative methods of preparing combustible casing materials falling within the scope of the present invention.

Example I

To 90 parts of a powder composition, which consists of:

	Percent
Nitrocellulose (13.15% N) -----	87.0±2.0
Dinitrotoluene -----	10.0±2.0
Dibutyl phthalate -----	3.0±1.0
Diphenylamine, 1 part added.	

and having a granulation range of from 0.025" to 0.034", was added a mixture consisting of 5 parts of Epon 828 and 5 parts of Versamid 125. The Epon 828 serves as a binder and is an epoxy resin manufactured by reacting epichlorohydrin with 2,2-bis(p-hydroxyphenyl) propane, while Versamid 125 which acts as a hardening agent is one of a group of Versamid polymers ranging from a polymer which is a liquid at room temperature to a polymer which is a solid at room temperature and which has a softening point of 190° C. They are prepared by the condensation of polymerized unsaturated fatty acids (e.g. dilinoleic acid) with aliphatic amines such as ethylene diamine. This composition of three ingredients was blended in a Sigma blade mixer until well blended. The composition was then cast into hollow tubes, or into the annulus between concentric tubes or in other suitable molds. The composition was then allowed to cure at temperatures from 50° F. to 212° F. for 45 minutes to 24 hours, depending on the curing temperature.

Example II

To 90 parts of a powder composition, which consists of:

Nitrocellulose (13.15% N) -----	100.00%.
Dinitrotoluene -----	8.00 parts added.
Potassium sulphate -----	1.00 part added.
Diphenylamine -----	0.7 part added.

was added a mixture of 2.5 parts of Epon 828 and 7.5 parts of Versamid 115. Epon 828 is described in greater detail in Example I and Versamid 115 is similar in composition and used interchangeably with the Versamid 125 described in Example I. This composition of three ingredients was blended in a Sigma blade type mixer until homogeneous. The composition was then cast into hollow tubes or other suitable molds. The composition was then allowed to cure at temperatures from 50° F. up to 212° F. for 45 minutes to 24 hours depending on the curing temperature.

Example III

To 87.5 parts of a powder composition, which is described in greater detail in Example I, having a granulation range of from 0.025" to 0.034", was added a mixture of 4 parts of Epon 828 and 0.8 part of Accelerator Z. Epon 828 is described in greater detail in Example I while Accelerator Z is a mixture of meta-phenylenediamine with a fluid resin. This composition of three ingredients was blended in a Sigma blade type of mixer until homogeneous. To the blend was then added 2.5 parts of a natural or synthetic fiber such as acetate rayon cut to ½" lengths. The mixing was then continued in the same mixer until the final formulation was well

blended. The formulation was then cast into the annulus between two concentric tubes and the composition was pressed at 4000 p.s.i. Finally, the formulation was allowed to cure for 24 hours at 140° F. The tube was then removed from the mold.

Example IV

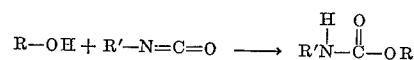
To 85 parts of a powder composition, which consists of:

	Percent
Nitrocellulose (13.15% N) -----	97.7
Potassium sulfate -----	0.75
Tin -----	0.75
Diphenylamine -----	0.80
Dinitrotoluene, 8.00 parts added.	

was added a mixture of 10 parts of Bakelite ERL 2795 resin binder and 2.5 parts Bakelite ERL 2793 hardening agent. The Bakelite ERL 2795 is an epoxy resin made by reacting a polyfunctional compound such as, for example 2,2-bis(p-dihydroxyphenyl) propane with epichlorohydrin. Bakelite ERL 2793 is an aliphatic amine used as a curing agent for Bakelite ERL 2795. This composition of three ingredients was blended in a Sigma blade mixer until homogeneous. To the blend was then added 2 parts of nitrocellulose fibers approximately 1" in length. The mixing was then continued until the formulation was well blended. The composition was then cast into a cylindrical mold and cured for 48 hours at room temperature. The cylinder was then removed from the mold.

The resins that are used may be any liquid polymer or monomer or a solid polymer or monomer that may be fused below the maximum temperature at which a propellant may be safely handled. This temperature varies with different propellants but may be defined as the temperature at which the propellants may explode. Suitable unsaturated polyesters may be prepared by reacting a compound containing two or more hydroxyl groups with an acid or acid anhydride containing at least two carboxyl groups and at least one unsaturated ethylenic double bond. Examples of compounds containing two or more hydroxyl groups are ethylene glycol, glycerol, pentaerythritol, propylene glycol, butanediol-1,4 and others. Examples of compounds containing two or more carboxyl groups and at least one unsaturated bond are maleic anhydride, maleic acid, fumaric acid, and others. In addition, other dicarboxylic acids or acid anhydrides (e.g. succinic acid, adipic acid, etc.) are simultaneously reacted with the above mentioned hydroxyl and carboxyl containing compounds to modify the properties of the resulting unsaturated polyester. The unsaturated polyester is then blended with a crosslinking agent such as styrene or diallyl phthalate. The crosslinking reaction is made to proceed under the influence of heat and/or a peroxide catalyst agent.

Polyurethane resins such as may be used in the present invention are formed when hydroxyl-containing compounds react with diisocyanates. The hydroxyl-containing compounds may be glycols, polyols, hydroxyl-containing polyesters or polyethers. The reaction may be simply depicted for illustrative purposes by monofunctional reactants as follows:



When polyfunctional chemicals are used, polymers are formed. The diisocyanate used is usually one or a mixture of the tolylene diisocyanate group of isomers. However, other diisocyanates may be used. An alternate method of preparing polyurethane is by pre-reacting a polyester with an excess of diisocyanate and then crosslinking the residual isocyanate groups with an amine or other compound containing a reactive hydrogen.

Epoxy resins such as may be used in the present invention may be prepared by condensation of epichloro-

$$(n+2) \text{CH}_2-\overset{\text{O}}{\text{CH}}-\text{CH}_2\text{Cl} + (n+1) \text{NaO}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{ONa} \longrightarrow$$

$$\text{CH}_2-\overset{\text{O}}{\text{CH}}-\text{CH}_2-(\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{O})_n$$

From the above examples and disclosure it is apparent that compositions made in accordance with this invention are capable of being formed or shaped into tubes, solid cylinders or other shapes by the use of appropriate molds. The product resulting thereby is a combustible material 60 suitable for use for such items as combustible cartridge cases, combustible primers, combustible initiators and other items where the combustion of the item in use is desirable or required. By the judicious selection of ingredients, the compositions can be made ballistically 65 smokeless.

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