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COMBUSTIBLE CARTRIDGE CASE OF FELTED FIBROUS MATERIAL WITH SYNTHETIC RESIN AND PROCESS**George E. Brown, Fairfax County, Va., assignor to Atlantic Research Corporation, Fairfax County, Va., a corporation of Virginia****No Drawing. Filed Apr. 26, 1965, Ser. No. 451,075
14 Claims. (Cl. 102-43)**

This invention relates to a new and improved combustible, shaped, felted, and fibrous nitrocellulose product and to the method for its preparation. More specifically, it relates to an improved combustible casing material for propellant and explosive powders and grains. Still more particularly, it pertains to a combustible cartridge casing material having superior physical properties.

Consumable cartridge casings made of felted cellulose fibers admixed with sufficient nitrocellulose fibers to make the casings combustible are known. Such casings are prepared by dispersing the fibers in a liquid in the form of a thick slurry and in the presence of a binder, preferably a synthetic organic resin, depositing the slurry on a casing form, removing the bulk of the liquid, compacting the fibers, and heating the deposited casing to dry it and to cure the resin binder. The resultant casing product is a fairly rugged container which exhibits many advantages over comparable metal casings. See for example, Ordinance, vol. XLVII, No. 254, September-October 1962, pages 231-234.

One of the serious problems encountered in preparation of a combustible casing suitable for munition type applications is that of achieving high tensile strength in the casing without significantly impairing the high porosity needed in the casing wall to obtain efficient combustion of the casing material. This invention provides an effective means for solving the foregoing problem.

Broadly speaking, the invention comprises subjecting a cured casing of the type described above to a solvating treatment with solvent for nitrocellulose for a period of time sufficient to permit penetration of the solvent into the pores of the casing, retaining the solvent in the pores until at least outer surfaces of the nitrocellulose fibers of the casing are solubilized, or tackified, and then removing the solvent.

The treated casing is a product having highly increased tensile strength, load bearing capacity and rigidity. This casing is able to withstand handling and shock with far less danger of damage than is experienced with untreated casings.

The advantageous increase in physical properties of the product of the invention depends in part on the type of synthetic organic resin binder which is present in the casing; in part on the solvent which is used to treat the casing; in part on the method of contacting of the casing with the solvent, e.g., by dipping, spraying, or vapor treatment; in part on the temperature of the treating process; and in part on the time duration of contact during treatment.

Binders of the synthetic organic resin type are commonly used in the manufacture of felted cellulose-nitrocellulose products from fibers. Not all resins are effectively suited for this purpose, since the binder resin must be compatible with the nitrocellulose and must not interfere with the combustion of the product, especially if the product is intended for use as a combustible cartridge casing. For the practice of the present invention, the binder present in the untreated product also should be one which does not seriously impair the solvation of the nitrocellulose fibers by the solvent being used.

A suitable binder material is, for example, one derived from a water-dispersed thermosetting adhesive resin com-

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position comprising a self-reactive, aqueous emulsion copolymer containing at least 90%, by weight, of vinyl acetate together with at least one other polymerizable comonomer containing at least one functional group selected from the group consisting of the glycidyl, methylol, including alkyl methylol, ureido, including alkylene ureido, hydroxyl, amine, carboxyl and alkoxy carbonyl groups. Binders of this type are disclosed and claimed in the co-pending application of DeFries and Godfrey, Serial No. 450,215, filed April 22, 1965. An example of such binder is copolymer of vinyl acetate in combination with methyl methacrylate in the ratio of 96:4 parts by weight.

It should be understood that this invention is not directed to a novel binder material. However, the binder which is already present in the untreated product must be duly considered, since the binder constitutes from about 15 to 35% of the cured casing material. The binder can be soluble in the solvent used. But it must neither be so soluble that it is extracted by the solvent, nor so insoluble that it prevents the solvent from solvating the nitrocellulose fibers held together by the binder. In the event that the solvent were to extract much of the binder, the form as well as the combustible characteristics of the product could be adversely altered. Also, were the binder material removed and the cellulose fibers held together solely by the solvated, dried nitrocellulose fibers, the resulting product would be brittle and substantially non-porous, and consequently impaired for use as a combustible cartridge casing. Accordingly, the invention is best practiced with a casing material made with a synthetic organic resin binder which preferably is only moderately soluble in the solvent system used.

The solvent used to practice the invention must be a solvent or solvent system which dissolves or solvates nitrocellulose fibers in the presence of the particular binder used to bind the untreated product. Nitrocellulose is known to be soluble in a variety of true solvents, chief among which are esters such as ethyl, butyl, and amyl acetates; ketones such as acetone, methyl ethyl ketone, and methyl isobutyl ketone; specific alcohols, such as methanol; and amides, such as ethyl amide. Nitrocellulose is also known to be solvated by solvent materials which are used as diluents with the above true solvents. Examples of the diluent materials are specific alcohols, e.g., ethanol, butanols; aliphatic hydrocarbons, e.g., hexane, heptane, octane; and aromatic hydrocarbons, e.g., toluene, xylenes. The solvent used, accordingly, can be any of the true solvents or mixtures thereof, e.g., acetone with methanol, and any mixture of a true solvent and a diluent, e.g., methanol with n-butanol. Acetone is preferably used as the solvent.

The amount of solvent used is not critical except that sufficient solvent should be used to cause adequate solvation of the nitrocellulose fibers in the casing so that upon removal of the solvent the nitrocellulose and cellulose fibers bond with each other. The treated casing is left in a significantly strengthened condition insofar as physical properties are concerned, and its porosity is not destroyed or detrimentally altered.

The method used in treating the product with solvent will depend somewhat on the form of the product. The product can be in the form of flat sheet, tape of suitable thinness for rolling, hollow forms, tubing, foraminous sheets and objects, and specific molded shapes, such as that of a rocket tube or of a cartridge casing. The product can be dipped into a solvent for an experimentally predetermined adequate time, removed from the dip bath, allowed to drain and then dried at an appropriate temperature. Alternatively, the product can be passed through a spray chamber and one or more surfaces or all surfaces subjected to a solvent spray, followed by the drying step after allowing an appropriate time for solva-

tion to take place. Also, the product can be exposed to solvent vapor in an enclosed vapor chamber. Other methods will be apparent to those skilled in the coating and impregnating arts.

The temperature of carrying out the process is not critical. However, temperatures higher than ambient preferably are used in order to accelerate solvation and subsequent removal of the solvent.

The time duration of contact must be controlled to provide adequate time for solvation to occur. However, prolonged contact of the nitrocellulose with solvent, particularly at an elevated temperature, can result in extraction of nitrocellulose or binder or both into the solvent and can cause degradation of the product both as to strength and as to its combustible properties.

In view of the highly combustible character of the product, due precautions must be taken to avoid the hazards of fire and explosions present during all phases of the processing. Usual practices followed by those skilled in the art should be strictly adhered to.

The advantages resulting from the practice of the invention are shown in the table where the test results of Example 1, obtained with a combustible cartridge casing which was not treated by the process of the invention, are compared with test results of Examples 2-10, obtained with solvent treated cartridge casings.

The cartridge casings of Examples 1-10 were made by the same process and each had the following nominal composition:

Component:	Weight, percent
Nitrocellulose (10.5-13.5% N)	57
Kraft fiber	14
Resin binder solids (copolymer of vinyl acetate)	23
Diphenylamine	2
Residual water	4

Casings in Examples 2-6 were dipped into the solvent at room temperature for about 20 seconds and allowed to dry at room temperature.

Casings in Examples 7-9 were exposed to acetone vapors at the boiling temperature of acetone at atmospheric pressure for varying periods of time, i.e., from 60 to 240 seconds.

The casing in Example 10 was sprayed with acetone with a pressure-fed paint spray gun with the tank pressure set at 18 to 20 p.s.i. with 15 to 20 p.s.i. pressure at the nozzle. The casing was sprayed and dried at room temperature.

The wall thickness of each casing was substantially the same as that of Examples 1, i.e., about 0.160". During treatment, some shrinkage occurs. The acetone dipped casings of Examples 2 and 3 underwent a wall thickness shrinkage of about 0.037 inch. This is not considered significant from the standpoint of operation of the process. However, where dimensions are critical, the shrinkage must be taken into account in preparing dies and molds. The sprayed casings underwent a wall thickness shrinkage of about 0.01 inch.

From Examples 2 and 3 it is seen that the acetone dip treatment increases ultimate stress, i.e., tensile strength, over 100% over that of the untreated casing of Example 1 despite the greater thickness of the latter casing. The stiffness of the treated casing is more than doubled, as shown by the Young's modulus data. The load bearing capacities are increased by 54-60%.

Example 4 shows that methanol is a good solvent for practice of the process but not as good as acetone.

Examples 5 and 6 show that n-butanol and isopropanol are not as advantageously effective as methanol.

Examples 7-9 show that the vapor method of treatment is not as efficient as the dip method, timewise.

Example 10 shows that the spray method also is less efficient than the dip method in improving resistance to stress and to load bearing capacity.

The treated casing materials of Examples 2-10 burned rapidly and cleanly on ignition.

Example 11

A series of about 0.160" wall thickness combustible cartridge cases having a nominal composition of 40 parts nitrocellulose fibers (10.5-13.5% N), 9 parts kraft fibers, 49 parts of the same synthetic organic resin binder as used in Examples 1-10, 1.4 parts of diphenylamine and a negligible amount of residual water were tested before and after treatment for 20 seconds with acetone by the dipping, or immersion, method. The following average results were obtained on samples cut from the walls, which were about 0.133" in thickness after the treatment:

	Max. Load, lbs.	Ultimate Stress, p.s.i.	Young's Modulus
Before	132	1,986	129,800
After	151	2,227	153,600
Percent Increase	10.4	14.0	11.8

Burning rate was slower than that in Examples 1-10.

From Example 11 it is to be noted that the ratio of binder to fibers is 1:1 and that, although initial values are relatively high compared to those of casings of Examples 1-3, increases in load bearing capacity, ultimate stress, and rigidity are relatively low. The reason for the low increases is believed due to the presence of the high amount of binder, which makes solvation of the nitrocellulose more difficult than that occurring in the casings used in Examples 1-10 where the binder to fibers ratio is 1:3.

Example 12

Wall samples from a series of about 0.160" thick combustible cartridge casings having a nominal composition of 75 parts nitrocellulose fibers (10.5-13.5% N), 20 parts kraft fibers, 3 parts diphenylamine and 2 parts water (no synthetic organic resin binder being present) were

TABLE

Ex. No.	Wall Thickness	Solvent	Time of Exposure, seconds	Type of Exposure	Test Data at 73° F.			Percent Increase Over Ex. No. 1		
					Max. Load, lbs.	Ultimate Stress, p.s.i.	Young's Modulus	Max. Load, lbs.	Ultimate Stress	Young's Modulus
1	.161	None	None	None	54.7	676	43,950	-----	-----	-----
2	.123	Acetone	20	Dip	84.5	1,371	95,650	54.3	101.8	102.5
3	.125	do	20	Dip	87.5	1,405	118,500	60.0	108.0	170.0
4	.141	Methanol	20	Dip	70.5	988	99,500	29.0	47.5	102.9
5	.159	n-Butanol	20	Dip	56.0	709	62,600	2.3	4.8	43.0
6	.165	Isopropanol	20	Dip	58.2	701	60,000	6.3	3.8	36.8
7	.147	Acetone	240	Vapor	69.5	943	173,000	27.0	39.5	293.0
8	.154	do	120	do	65.8	851	64,100	20.1	26.0	41.5
9	.149	do	60	do	59.3	797	64,500	18.5	18.0	47.0
10	.145	do	Saturated	Spray	-----	1,150	-----	-----	70.0	-----

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tested before and after treatment for 20 seconds by dipping in acetone. The wall thickness averaged 0.09" after treatment. The following results were obtained:

	Max. Load, lbs.	Ultimate Stress, p.s.i.	Young's Modulus
Before.....	54.7	676	43,950
After.....	30	1,147	88,700
Percent Increase.....	(-)28.7	70	100.2

The treated product was brittle compared to the untreated, as can be seen from the decrease in load bearing capacity of the treated material. Thus, while the tensile strength and stiffness of the treated product were improved by the acetone treatment, the product was made brittle. Porosity of the product was reduced, as evidenced by the wall thickness shrinkage experienced, in comparison to samples of treated material bound as in Examples 1-11.

While the invention has been described in its preferred embodiments it is to be understood that it may be practiced in other embodiments within the scope of the claims as will be clear to those skilled in the art.

I claim:

1. The process which comprises subjecting a combustible, shaped, felted, and fibrous material consisting essentially of nitrocellulose fibers, cellulose fibers and synthetic organic resin binder therefor to a solvating treatment with solvent for nitrocellulose for a period of time sufficient to solubilize at least the outer surfaces of said nitrocellulose fibers, and then removing the solvent.

2. The process according to claim 1 in which the solvent is a true solvent for nitrocellulose.

3. The process according to claim 2 in which the solvent is a ketone.

4. The process according to claim 3 in which the solvent is acetone.

5. The process according to claim 2 in which the solvent is methanol.

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6. The process according to claim 2 in which the solvent is an ester.

7. The process according to claim 1 in which the solvent is a mixture of a true solvent and a diluent solvent.

8. The process according to claim 7 in which the diluent solvent is a butanol.

9. The process according to claim 1 in which the material is in the shape of a combustible cartridge casing.

10. The process according to claim 1 in which the material contains from about 15 to 35% of a cured resin binder derived from a self-reactive copolymer containing at least 90%, by weight, of vinyl acetate together with at least one other polymerizable comonomer containing at least one functional group selected from the group consisting of the glycidyl, methylol, ureido, hydroxyl, amine, carboxyl and alkoxycarbonyl groups.

11. A combustible shaped, felted, fibrous material comprising a minor amount of synthetic organic resin binder and a major amount of nitrocellulose fibers subjected to a solvating treatment in accordance with the process of claim 1.

12. A combustible shaped, felted, fibrous material comprising a minor amount of synthetic organic resin binder and a major amount of nitrocellulose fibers subjected to a solvating treatment in accordance with the process of claim 10.

13. The combustible material of claim 11 in the form of a cartridge casing.

14. The combustible material of claim 12 in the form of a cartridge casing.

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