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## METHOD FOR THE PREPARATION OF PROGRESSIVE-BURNING SMOKELESS POWDER AND PRODUCT THEREOF

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This invention relates to an improved method for the preparation of progressive-burning double base smokeless powder and more particularly to an improved method of coating double base smokeless powder using deterrent material and to the product so made.

In order to render possible, close control of the burning rate of smokeless powder and produce a high velocity of the projectile without high breech pressures, it has been customary to coat the grains of the smokeless powder with a deterrent material, explosive or non-explosive, which will retard the initial burning rate of the powder grains. Such coating material penetrates the powder grains more or less, so that as the powder burns, the successively exposed surfaces contain gradually less and less of the deterrent material, thus causing the combustion of the grains to proceed with increasing speed.

It has been the general practice heretofore to coat double base powders at relatively high temperatures, but this procedure has been open to a number of objections, chief among which was the fact that powders so coated had a tendency to give high breech pressures when fired at low temperatures. This is a serious disadvantage and while many attempts have been made to improve this defect of prior art powders, none have met with any appreciable success. It is the object of this invention to provide a process of making a progressive-burning double base smokeless powder which does not produce excessive breech pressures when fired at low temperatures.

In accordance with my invention, I produce a progressive-burning double base smokeless powder in which the pressure increases usually obtained when it is fired at low temperatures are largely or wholly eliminated by applying to the smokeless powder at a temperature less than 55° C. preferably at a temperature from about 10° C. to about 50° C., a deterrent material which is a non-solvent for the nitrocellulose in the powder but compatible therewith admixed with either a volatile or a non-volatile solvent for said nitrocellulose.

The exact mechanism whereby the improvement is obtained by coating with my deterrent combination at temperatures less than 55° C. is not known. It is believed that the excess heat in high temperature coating procedures affects the colloidal structure of the powder grain in a manner so as to weaken its strength, that is, it decreases its resistance to shattering due to the shock of the primary explosion, and of course the smaller the particles, the faster is their rate of burning. Whatever may be the mechanism, however, the results clearly show that pressure increases due to the firing of the powder at sub-zero temperatures are practically completely eliminated by proceeding in accordance with my process.

I may, if so desired, extend the mixture of a volatile or non-volatile solvent and the non-solvent deterrent with a volatile vehicle which is not a solvent for the smokeless powder grains such as benzene, ethyl alcohol, petroleum spirits and so forth, in order to render the above said mixture more fluid and to cause it to come into more intimate contact, and then subsequently remove this vehicle by evaporation. In general, I prefer applying the non-solvent deterrent in solution in a volatile solvent extended with a diluent of the type before mentioned, but in the case of certain types of powder, where greater penetration of the coating is necessary to decrease the initial burning speed, without causing too great a difficulty of ignition, I prefer to use a minimum amount of a non-volatile solvent for the smokeless powder admixed with a non-solvent deterrent both applied in a solution in a volatile solvent for the smokeless powder and a diluent. Alternatively, I may extend the mixture of a volatile or non-volatile solvent and a non-volatile deterrent by forming an aqueous emulsion thereof with a suitable emulsifying agent. I may also form an aqueous emulsion of the volatile vehicle extended mixture above shown. The particular method used for rendering the above mixture more fluid will depend on which is more convenient and desirable for the particular deterrent and smokeless powder in question.

In using my process, it may also be desirable to add water near the end of my coating procedure in order to prevent the grains of powder from adhering to each other. Near the end of the coating process a very concentrated solution remains on the powder grains, which on further evaporation causes the coating material to be deposited on the surface of the powder grain, resulting in the adherence of the grains to each other. Now I have found that if water is added at this stage, that is, just before serious clustering begins, each grain will be surrounded by a film of water which greatly reduces the stickiness of the grains. Heating can then be continued either in the sweetie barrel, or in the dry house, to cause the penetration of this surface material into the grain and thus avoid the formation of clusters.

As examples of deterrents which I may utilize to coat the grains of double base smokeless powder in accordance with this invention I may use the alkyl esters of the fatty acids, as, alkyl esters of ricinoleic acid, alkyl esters of polymerized ricinoleic acid, etc.; terpene phthalates; rosin esters, as monohydric esters of abietic acid, polyhydric alcohol esters of abietic acid, monohydric alcohol esters of pimaric acid, polyhydric alcohol esters of pimaric acid; synthetic lacquer resins as

the modified or unmodified polyhydric alcohol-polybasic acid resins (alkyds, Rezyls), phenol formaldehyde type resins, etc.; rosins, as wood rosin, gum rosin, etc.; hydrogenated rosins, as hydrogenated wood rosin, hydrogenated gum rosin, etc.; and the like. Thus, I may use butyl ricinoleate, butylacetyl ricinoleate, butyl ester of polymerized ricinoleic acid, dibornyl phthalate, methyl abietate, ethyl abietate, hydrogenated methyl abietate, hydrogenated ethyl abietate, ester gum, hydrogenated ester gum, modified or unmodified glycerol-phthalate resin, oil modified phenol-formaldehyde type resins, glycerol sebacate, glycol sebacate, glycerol-glycol sebacate, modified or unmodified ethylene glycol terpinene maleic anhydride resins, modified or unmodified diethylene glycol terpinene maleic anhydride resins, modified or unmodified triethylene glycol terpinene maleic anhydride resins, modified or unmodified glycerol terpinene maleic anhydride resins, etc.

As examples of the non-volatile solvent materials which I may use with the above mentioned deterrents, I may use the alkyl phthalates as for example, diethyl phthalate, dibutyl phthalate, diamyl phthalate, etc.; alkylphthalyl alkylglycollates, as for example, butylphthalyl butylglycollate, ethylphthalyl ethylglycollate, etc.; substituted ureas, as for example, symmetrical diethyldiphenyl urea, symmetrical dimethyldiphenyl urea, symmetrical ethylmethyldiphenyl urea, etc.; alkyl tartrates such as dibutyl tartrate, etc.; alkyl citrates such as triethyl citrate, etc.; adipates such as cyclohexanol adipate; and lower alkyl esters of benzoic acid such as ethyl and methyl ortho-benzoylbenzoate.

As examples of the volatile solvent materials which I may use with the above mentioned deterrents, I may use ethyl acetate, butyl acetate, mixtures of alcohol and ether and any others having a solvent effect on the nitrocellulose in the smokeless powders and having a boiling point from about 35° C. to about 180° C., preferably from about 70° C. to about 130° C.

As illustrative of my invention I may coat 100 parts by weight of a tubular grain double base rifle powder at a temperature less than about 55° C., preferably at a temperature about 10° C. to about 50° C. with between about 0.5 to about 10 parts by weight of a mixture comprising 25% to 95% of a deterrent, non-volatile and non-explosive and which is a non-solvent for the nitrocellulose but compatible therewith and 5% to 75% of a non-volatile non-explosive solvent plasticizer for the nitrocellulose, said mixture being dissolved in 3 parts to 50 parts by weight of a volatile vehicle having substantially no solvent action on the nitrocellulose. In place of the non-volatile non-explosive solvent plasticizer, I may use a volatile solvent for the nitrocellulose.

Alternatively, I may coat 100 parts by weight of a tubular grain double base smokeless powder, suitable for use in high powered rifles, at the same temperatures as above shown, with between about 0.5 part to about 10 parts by weight of a mixture comprising 25% to 95% of a deterrent, non-volatile and non-explosive and which is a non-solvent for the nitrocellulose but compatible therewith and 5% to 75% of a non-volatile, non-explosive solvent plasticizer for the nitrocellulose, said mixture being emulsified in 3 to 50 parts by weight of an aqueous solution of water-soluble carbohydrate ether, such as for example, methyl cellulose. In place of the non-volatile, non-explosive solvent plasticizer, I may also use a volatile solvent for the nitrocellulose.

As another illustration, I may coat 100 parts by weight of a tubular grain double base smokeless powder, suitable for use in high powered rifles at the same temperatures as above mentioned, with between about 0.5 part to about 10 parts by weight of a deterrent, non-volatile and non-explosive which is a non-solvent for the nitrocellulose but compatible therewith dissolved in 1 part to 20 parts by weight of a volatile solvent for nitrocellulose and 3 parts to 50 parts by weight of a volatile vehicle which is a non-solvent for the powder. Alternatively, instead of the non-solvent volatile vehicle, I may use 3 parts to 50 parts by weight of an aqueous solution of methyl cellulose and apply the above mixture in the form of an emulsion.

As a further illustration I may coat 100 parts by weight of a tubular grain double base smokeless powder suitable for use in high powered rifles with between about .5 part to about 10 parts by weight of a mixture comprising 25% to 95% of a deterrent, non-volatile and non-explosive and which is a non-solvent for the nitrocellulose but compatible therewith and between about 5% to about 75% of a non-volatile solvent plasticizer for the nitrocellulose, 100 parts by weight of said mixture being dissolved in 50 parts to 300 parts by weight of a volatile solvent for the nitrocellulose. This solution may be extended with a volatile vehicle or emulsified as described in the modifications as above. The amount of volatile solvent used will depend on the type of powder, the degree of penetration desired, and the amount of deterrent used.

Powder grains may be coated in any convenient apparatus, for example, in a sweetie barrel and after coating may be removed to a dry house for several days, then glazed with graphite and screened to remove any coarse or fine material. The time of coating will depend upon the type of powder coated and the results desired and may vary anywhere from 15 minutes to 6 hours, but in general will vary from about 30 minutes to about 2½ hours.

Having described my invention in a general manner, I will now proceed to a more detailed description by reference to the following examples:

*Example 1*

Four hundred and fifty-three parts by weight of smokeless powder containing 20% nitroglycerine are pressed through a .041 inch die having a .015 inch pin, the resulting strands being cut into 21 pellets per inch. These smokeless powder grains are placed in a sweetie barrel and to them are added 3.9 parts by weight of butylacetyl ricinoleate and 3.9 parts by weight of ethyl ortho-benzoylbenzoate dissolved in 80 parts by weight of 95% ethyl alcohol. The powder is then tumbled in the sweetie barrel with a coating solution for ½ hour at 40° C. It is then dried, graphited and screened to remove coarse and fine particles. This powder when fired in a .30 caliber gun using a 170 grain bullet at a temperature of —47° F. gave an average breech pressure of only 6,700 pounds per square inch higher than when fired at 76° F.

The same powder coated in an identical manner except that a coating temperature of 60° C. is used, when fired in the same manner at —47° F. gave a breech pressure 36,300 pounds per square inch higher than when fired at 76° F.

*Example 2*

Fifty parts by weight of the powder in Example 1, with the same granulation, is coated with 0.5 part by weight of wood rosin and 0.65 part by weight of ethyl ortho-benzoylbenzoate dissolved in 6 parts by weight of 95% alcohol and 0.75 part by weight of butyl acetate. This powder was tumbled in the sweetie barrel with the deterrent solution for 45 minutes at 40° C., removed therefrom, dried, graphited, and screened. This powder when fired in a .30 caliber cartridge with a 170 grain bullet at —40° F. gave a breech pressure 300 pounds per square inch lower than when fired at 82° F.

*Example 3*

Nine hundred and six parts by weight of the same base powder as in Example 1 and of the same granulation, was coated with 10 parts by weight of wood rosin dissolved in 18.1 parts by weight of secondary butyl acetate and 120 parts by weight of ethyl alcohol. This powder was tumbled in the sweetie barrel with the coating solution for 45 minutes at 40° C., removed therefrom, dried, graphited, and screened. This powder when fired in a .30 caliber cartridge with a 110 grain bullet at a temperature of —42° F. gave a breech pressure 2,100 pounds per square inch higher than when fired at 80° F.

*Example 4*

Nine hundred and seven parts by weight of the same base powder as in Example 1 and granulated in the same manner, was coated with 9.1 parts by weight of wood rosin and 11.3 parts by weight of ethyl ortho-benzoylbenzoate dissolved in 91 parts by weight of 95% alcohol, and 13.6 parts by weight of butyl acetate. The powder was coated in the sweetie barrel with this deterrent solution for ½ hour at 40° C., dried in the dry house for 3 days at 55° C., glazed and screened in the usual manner.

*Example 5*

The same powder as in Example 4 was treated in the manner indicated in Example 4 by using a coating temperature of 50° C.

*Example 6*

Treatment the same as in Example 4 but using a coating temperature of 60° C.

*Example 7*

Treatment the same as in Example 4 but using a coating temperature of 70° C.

Powders made as shown in Examples 4–7 inclusive when fired in a .30 caliber cartridge with a 170 grain bullet show the following characteristics. It should be noted in the following table that the velocities shown are instrumental velocities determined over a 150 foot range.

| Example | Charge | Velocity | Mean pressure | Max. pressure | Powder temp. |
|---|---|---|---|---|---|
| | | | | | ° F. |
| 4 | 28.0 | 2079 | 35,900 | 39,500 | 82 |
| 4 | 28.0 | 2030 | 33,600 | 36,400 | —40 |
| 5 | 30.0 | 2117 | 35,800 | 37,700 | 86 |
| 5 | 30.0 | 2093 | 35,900 | 41,300 | —40 |
| 6 | 29.3 | 2105 | 34,800 | 37,700 | 86 |
| 6 | 29.3 | 2097 | 42,100 | 57,400 | —40 |
| 7 | 28.6 | 2118 | 38,700 | 42,100 | 87 |
| 7 | 28.6 | 2165 | 58,200 | 67,700 | —40 |

By coating smokeless powder according to my process, as illustrated in the above examples, it is apparent that the powders coated with my deterrent mixtures at temperatures less than 55° C. produce breech pressures when fired at sub-zero temperatures which are not substantially greater than those produced when the same powder is fired at ordinary temperatures.

It will be understood that where I have referred to a compound as being a non-solvent for nitrocellulose, I mean a compound which, by reason of its relatively low content of chemical groups, which are known to promote solvent action, its high molecular weight, its high viscosity at temperatures to which the compound may be subjected, or its structural arrangement, does not dissolve nitrocellulose of the degree of nitration used in a particular case at a measurable rate of solution.

It will be understood that the details and examples hereinabove set forth are illustrative only and that the invention as herein broadly described and claimed is in no way limited thereby.

This application is a continuation-in-part of my application Serial No. 152,269, filed July 6, 1937.

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

1. A method of preparation of progressive-burning, double base smokeless powder, characterized by producing breech pressures when fired at sub-zero temperatures which are not substantially greater than those produced when fired at ordinary temperatures, which comprises coating double base smokeless powder grains at a temperature less than about 55° C. with an admixture of a non-volatile, non-explosive organic material which is a non-solvent for the nitrocellulose but compatible therewith and a solvent for said nitrocellulose.

2. A method of preparation of progressive-burning, double base smokeless powder, characterized by producing breech pressures when fired at sub-zero temperatures which are not substantially greater than those produced when fired at ordinary temperatures, which comprises coating double base smokeless powder grains, at a temperatures less than about 55° C., with an admixture of an alkyl ester of a higher fatty acid and a solvent for said nitrocellulose.

3. A method of preparation of progressive-burning, double base smokeless powder, characterized by producing breech pressures when fired at sub-zero temperatures which are not substantially greater than those produced when fired at ordinary temperatures, which comprises coating double base smokeless powder grains, at a temperature less than about 55° C., with an admixture of an alkyl ester of ricinoleic acid and a solvent for nitrocellulose.

4. A method of preparation of progressive-burning, double base smokeless powder, characterized by producing breech pressures when fired at sub-zero temperatures which are not substantially greater than those produced when fired at ordinary temperatures, which comprises coating double base smokeless powder grains, at a temperature less than about 55° C., with an admixture of butylacetyl ricinoleate and a solvent for nitrocellulose.

5. A method of preparation of progressive-burning, double base smokeless powder, characterized by producing breech pressures when fired at sub-zero temperatures which are not substantially greater than those produced when fired at ordinary temperatures, which comprises coating double base smokeless powder grains, at

temperatures less than about 55° C., with an admixture of rosin and a solvent for nitrocellulose.

6. A method of preparation of progressive-burning, double base smokeless powder, characterized by producing breech pressures when fired at sub-zero temperatures which are not substantially greater than those produced when fired at ordinary temperatures, which comprises coating double base smokeless powder grains, at temperatures less than about 55° C., with an admixture of rosin and a lower alkyl ester of benzoylbenzoic acid.

7. A method of preparation of progressive-burning, double base smokeless powder, characterized by producing breech pressures when fired at sub-zero temperatures which are not substantially greater than those produced when fired at ordinary temperatures, which comprises coating double base smokeless powder grains, at temperatures less than about 55° C., with an admixture of rosin and ethyl ortho-benzoylbenzoate.

8. A method of preparation of progressive-burning, double base smokeless powder characterized by producing breech pressures when fired at sub-zero temperatures which are not substantially greater than those produced when fired at ordinary temperatures which comprises coating double base smokeless powder grains at a temperature less than about 55° C. with an admixture of rosin and butyl acetate.

9. A double base smokeless powder coated with an admixture of a non-volatile, non-explosive organic materials which is a non-solvent for the nitrocellulose but compatible therewith and a non-volatile solvent for said nitrocellulose, said coated smokeless powder being progressive-burning and being characterized by producing breech pressures when fired at sub-zero temperatures which are not substantially greater than those produced when fired at ordinary temperatures.

10. A double base smokeless powder coated with an admixture of an alkyl ester of a higher fatty acid and a non-volatile solvent for the nitrocellulose, said coated smokeless powder being progressive-burning and being characterized by producing breech pressures when fired at sub-zero temperatures which are not substantially greater than those produced when fired at ordinary temperatures.

11. A double base smokeless powder coated with an admixture of an alkyl ester or ricinoleic acid and a non-volatile solvent for the nitrocellulose, said coated smokeless powder being progressive-burning and being characterized by producing breech pressures when fired at sub-zero temperatures which are not substantially greater than those produced when fired at ordinary temperatures.

12. A double base smokeless powder coated with an admixture of butyl acetyl ricinoleate and a non-volatile solvent for the nitrocellulose, said coated smokeless powder being progressive-burning and being characterized by producing breech pressures when fired at sub-zero temperatures which are not substantially greater than those produced when fired at ordinary temperatures.

13. A double base smokeless powder coated with an admixture of rosin and a non-volatile solvent for the nitrocellulose, said coated smokeless powder being progressive-burning and being characterized by producing breech pressures when fired at sub-zero temperatures which are not substantially greater than those produced when fired at ordinary temperatures.

14. A double base smokeless powder coated with an admixture of rosin and a lower alkyl ester of benzoylbenzoic acid, said coated smokeless powder being progressive-burning and being characterized by producing breech pressures when fired at sub-zero temperatures which are not substantially greater than those produced when fired at ordinary temperatures.

15. A double base smokeless powder coated with an admixture of rosin and ethyl ortho-benzoylbenzoate, said coated smokeless powder being progressive-burning and being characterized by producing breech pressures when fired at sub-zero temperatures which are not substantially greater than those produced when fired at ordinary temperatures.

16. A double base smokeless powder coated with an admixture of butyl acetyl ricinoleate and ethyl ortho-benzoylbenzoate, said coated smokeless powder being progressive-burning and being characterized by producing breech pressures when fired at sub-zero temperatures which are not substantially greater than those produced when fired at ordinary temperatures.

ELLSWORTH S. GOODYEAR.