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METHOD OF MANUFACTURING SHAPED PROPELLANTS

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This invention relates to the production of shaped propellants and concerns particularly the preparation of molten mixtures of nitrocellulose, nitrated polyhydric alcohols and low-melting-point-nitro-compounds serving for manufacturing propellants and relates also to the treatment of these mixtures for producing the propellants therefrom.

It is known in the art of manufacturing propellants, such as ordnance and rifle gunpowder and propellant charges for rockets, to dehydrate a mixture of nitrocellulose, nitroglycerin or one or several similar nitrated polyhydric alcohols and water on a heated calender and thus by means of the nitrated polyhydric alcohols gelatinize the nitrocellulose. The gelatinized mixtures are again calendered to form thin skins and are then cut into bands or flakes or pressed through a nozzle into tubular form. This calendering takes much time and energy and is very dangerous due to the mass being friction-sensitive and combustible at high temperatures. Another disadvantage is that the resulting vapors of the nitrated alcohols inconvenience the calender operators.

In the manufacture of explosives i. e. of rapidly reacting explosive mixtures of chemical compounds with a gas development of bursting action this disadvantage can be eliminated by mixing the explosive ingredients in a molten state and by subsequently pouring the molten mass into molds, e. g. for shells or bombs. If this method is used in the manufacture of propellants i. e. of slowly reacting explosive mixtures of chemical compounds with a gas development ejecting the projectiles from a gun or rocket barrel, particularly of propellants containing nitrocellulose and nitrated polyhydric alcohols, there are difficulties resulting from the fact that, when the aqueous mixture prepared in the usual manner and containing e. g. nitrocellulose and diglycoldinitrate, is added to molten trinitrotoluene or to another molten nitro-compound, only part of the nitrocellulose is gelatinized so that no homogeneous solution is obtained.

Now, on the base of thorough experiments it has been discovered that the manufacture of melts containing nitrocellulose, aromatic nitro compounds and nitrated polyhydric alcohols for the use in propellants requires for obtaining homogeneous solutions that the nitrocellulose enriched with nitrated polyhydric alcohol has a certain water content which must amount to at least 18 per cent and, preferably, is chosen from 20 to 23 percent. If the water content of the mixture is too low, the nitrocellulose is not completely dissolved so that undissolved little lumps remain which have an adverse effect on the ballistic qualities of the powder. If, however, the water content of the mixture is exceedingly high, the melting process will take too much time and this fact will render the final product instable.

Experiments have further shown that, when mixing the nitrocellulose with the nitrated polyhydric alcohol, a low temperature must be maintained which does not exceed 18 centigrade, in order to prevent the nitrocellulose from gelatinizing before it is added to the melt, and to avoid the formation of lumps.

Based on these discoveries, melts serving for the manufacture of propellants are produced according to the invention by introducing into a molten nitrocompound a mixture consisting of nitrocellulose and of a nitrated polyhydric alcohol, having a water content of at least 18 percent and prepared at a temperature not exceeding 18 centigrade. In this way, not only the calendering work being otherwise usual for dehydrating the powder mixtures when manufacturing propellants is completely avoided but also a perfectly homogeneous solution capable of being easily cast is obtained without any formation of lumps.

It is advantageous to use for the powder mixture a nitrocellulose having a nitrogen content of below 12.4 percent because a nitrocellulose with a higher nitrogen content than 12.4 percent results in melts which are very viscous even when the viscosity of the nitrocellulose is low; such viscous melts cannot readily be shaped or deaerated. Furthermore, it is important to effect the evaporation of the water during the dissolving process at a rate which will ensure a complete solution of the nitrocellulose in the melt.

Furthermore, experiments have proved that favorable results are obtained by using for the manufacture of propellants according to the invention a nitrocellulose which has been pre-treated in an autoclave to reduce its viscosity to such a degree that upon the determination of the viscosity in a Cochius-viscosimeter (7 mm.) at 18 centigrade, a 10 percent solution of the nitrocellulose in a mixture of butanol, butylacetate and toluene in the ratio of 3:4:5 will have a rate of flow from 15–20 seconds.

For dissolving the nitrocellulose mixed with a nitrated polyhydric alcohol I use nitro compounds which have a melting point below the decomposition temperature of nitrocellulose i. e. below 130 centigrade. Aromatic and aliphatic nitro compounds may be used; for instance, suitable aromatic nitro compounds are: di- or trinitrotoluene, di- or trinitrobenzene, di- or trinitrophenol, di- or trinitrophenylglycolethernitrate, tetranitromethylaniline, mononitronaphthalene, trinitronaphthalene, dinitrooxytoluene, pentanitrodiphenylamine, trinitrophenylglycine, trinitrophenylethanolamine, suitable aliphatic nitro compounds are e. g. dinitrodiethanolnitratoxamide, tetranitropentaerytrite, dioxyethylsulfodinitrate. Mixtures of these aliphatic and aromatic nitro compounds and nitrates may also be used for gelatinizing the nitrocellulose. As nitrated polyhydric alcohols e. g. nitroglycerin, diglycoldinitrate, nitrated methriol and similar nitrated alcohols may be employed for the melts prepared according to the invention. The nitrated polyhydric alcohols may partly be replaced by plasticizers.

Example I

In a kettle provided with a heating jacket, 53 kg. trinitrotoluene of 12.1 percent and a viscosity of 20 seconds, measured in a 3 percent acetone solution according to Cochius, are thoroughly mixed at 14 centigrade with 18 kg. diglycoldinitrate in an aqueous emulsion. This mixture is centrifuged and thus freed from the excess water so that a water content of 22 percent is obtained. The nitrocellulose enriched with the nitrated polyhydric alcohol is disintegrated in the usual manner and slowly added to the molten trinitrotoluene while stirring. Then the kettle is hermetically closed and the water is removed by evacuating. The dehydration must be controlled to ensure that the evaporation proceeds at about the same rate as the gelatinization because a too rapid evaporation will prevent a good gelatinization. The

thus obtained homogeneous melt, which may be easily cast, will be shaped in the usual manner.

The method of preparing according to the invention molten mixtures of nitrocellulose, nitrated polyhydric alcohols and nitro compounds for the manufacture of propellants may be improved by choosing a certain favorable ratio between the constituents of the mixtures, particularly in the case of large bodies of powder as applied, for instance, in propellant charges for rockets; there the formation of cavities provoking detonations during the deflagration has to be avoided at all events and, furthermore, the solidification of the molten mass must not take too long in spite of its large size. This improvement consists in the step of observing in the molten mixture between the aromatic or aliphatic nitro compound on the one hand, and the other mixture ingredients on the other hand, a fixed proportion kept within rather narrow limits and ranging from 1:1 to 3:2.

Experience has shown, that obtaining a complete solution of the nitrocellulose and, as a consequence thereof an entirely homogeneous propellant, which can be easily cast, is rendered very difficult, when the aromatic nitro compound content of the mixture, e. g. trinitrotoluene, is too low; on the other hand, with the nitro compound content exceeding 60 percent of the solution, the molten mixture exhibits, upon cooling after shaping, especially in the case of large powder bodies, a strong tendency to formation of cavities and fissures. Moreover, the solidified mass easily becomes brittle and this alone makes it practically useless. These disadvantages are noticed not only with trinitrotoluene, but also with other aromatic nitro compounds, such as trinitroglycolether or trinitromethylaniline.

Example II

In a kettle provided with a heating jacket, 530 kg. trinitrotoluene are melted at 80 centigrade. 280 kg. nitrocellulose with a nitrogen content of 12.1 percent are thoroughly mixed with 180 kg. diglycoldinitrate in an aqueous emulsion. The mixture is centrifuged and thus freed from the excess of water to a water content of 22 percent. The moist nitrocellulose enriched with diglycolnitrate is disintegrated in the usual manner and then slowly added to the molten trinitrotoluene while stirring. Finally, the kettle is hermetically closed and the water is removed by evacuating and the nitrocellulose dissolves.

Cooling of the propellant obtained by utilising the solubility of nitrocellulose in molten nitro compounds may be effected advantageously according to the invention by maintaining a certain temperature which will yield a finished product of gelatinised nitrocellulose containing the molten aromatic or aliphatic nitro compound in finest distribution and will allow the powder bodies formed from the molten mass to solidify without cavities and within the shortest possible time.

On the other hand, for obtaining the melt it was found useful to effect the dissolving of the nitrocellulose in a vacuum tank while stirring, in order to facilitate the removal of the air bubbles from the solution. Furthermore, with a view of obtaining as homogeneous a solution as possible and one of low viscosity, the temperature of the solution may be increased for a short period after the elimination of the water, and for dissolving the nitrocellulose in the molten nitro compound it is advisable to maintain a temperature which lies approximately 10 to 20 centigrade above the melting point of the nitro compound.

Example III

In a melting tank of 300 liters' capacity, provided with stirring equipment and enclosed by a heating jacket heated with hot water, I melt 100 kilograms trinitrotoluene (melting point approximately 80 centigrade). To the melt I add, gradually in measured doses, 70 kilograms

nitrocellulose, containing 30 percent water and 12 percent nitrogen enriched with dinitrodiglycol at the ratio of 3:2. By maintaining a temperature of 100 centigrade, the water will evaporate and as evaporation proceeds, the nitrocellulose will dissolve; after evaporation of the water is completed, a homogeneous melt will remain behind.

For eliminating the air bubbles, the melting tank is provided with hermetically-sealed lid and connected to a vacuum line after the addition of the moist nitrocellulose, enriched with dinitrodiglycol. For complete elimination of air bubbles from the mixture, the temperature is increased by approximately 10 centigrade at the end of the dissolving process. This rise in temperature will at the same time cause a decrease of the viscosity of the melt as it forms and this, in turn, will facilitate the shaping of the melt.

For shaping, the molten mass is poured into a mold which has a constant temperature of for instance 25 centigrade; care must be taken to maintain this temperature during the solidifying process of the mass and to prevent any decrease during the cooling process. By applying too low cooling temperatures, unpleasant over-coolings may easily occur which will lead to sudden crystallizing and cavity formation, whereby powder units with a deficient homogeneity will be obtained; on the other hand, the solidification process of the viscous molten mass will take too long when too high a temperature is maintained during the cooling step.

When manufacturing larger-sized powder units, such as the cylindric units applied as propellant charges for rockets, a supervision of the cooling process is required not only for temperature control; care must also be taken that the cooling of the cylindric unit will be effected from the bottom to the top and from the inside to the outside; otherwise, local concentrations of the mass will lead to formation of hollow spaces inside the unit during the cooling process.

In order to shorten as much as possible the period of the solidification of the molten powder mixtures, which sometimes requires as much as 20 to 30 hours, especially in the case of manufacturing large bodies of powder having large wall thickness, and yet to avoid with security the risk of formation of cavities and irregularities during crystallisation, which would have an adverse effect on the ballistics, the method based on the introduction of nitrocellulose and polyhydric alcohol in a molten nitro compound may be improved by the step of cooling down the molten mixture below the solidification temperature and by transforming this undercooled melt into the desired shape. In this way, the solidification period is reduced to a fraction of the time otherwise required and is cut down to only a few minutes, without formation of hollow spaces or interior tensions within the propellant.

This undercooling of the molten mixture is based on the discovery, which resulted from extensive experimentation, that the molten powder mixtures possess the property to pass, when being cooled down below the solidification point, for a time of transition into an instable state in which they exhibit a viscous nature, and are therefore still easily cast. The shaping of the molten mass being in a semi-plastic state may be effected in the usual manner by means of an extruder, a screw press, or similar devices. The best way is to shape the molten powder mixture before its solidification is quite complete so as to allow the formed body to solidify at room temperature without further modification of its shape. The formed units may preferably be left standing for a short time at room temperature.

Example IV

A mixture of 53 parts of trinitrotoluene, 28 parts of nitrocellulose with a nitrogen content of 12 percent, 18 parts of diglycol and 1 percent of a stabilisator are melted at 80 centigrade to form a homogeneous mass. This melt having a melting point of about 60 centigrade is cooled

down to a temperature of +30 centigrade which may be reached within 10 minutes in a pipe branched from the kettle. After the melt has cooled down it still shows plastic characteristics and may be shaped into any desired form, for instance into a tubular form, in a continuous process by means of an extruder.

Having described my invention, what I claim and desire to protect by Letters Patent is:

1. A method of manufacturing shaped propellants, which comprises preparing at a temperature between 0° and 180° C. a mixture consisting of nitrocellulose and of a nitrated polyhydric alcohol selected from the group consisting of glycols and glycerines at a ratio of nitrocellulose:alcohol of about 3:2 and having a water content of at least 18%, and then introducing said mixture into a molten nitro compound selected from the group consisting of dinitrotoluene, trinitrotoluene, dinitrobenzene, trinitrobenzene, dinitrophenol, trinitrophenol, ditrinitrophenylglycolethernitrate, trinitrophenylglycolethernitrate, tetranitromethylaniline, mononitronaphthalene, trinitronaphthalene, dinitrooxytoluene, pentanitrodiphenylamine, trinitrophenylglycine, trinitrophenylethanolamine, dinitrodiethanolnitratoxamide, tetranitropentaerytrite, dioxyethylsulfodinitrate and having a melting point below 130° C., thereafter shaping the propellant from the obtained molten mass, and solidifying the propellant.

2. The method according to claim 1, wherein a nitrocellulose having a nitrogen content from about 12 to below 12.4 percent is used for preparing the mixture of nitrocellulose and polyhydric alcohol.

3. The method according to claim 1, wherein the nitrocellulose used for said mixture with alcohol is a nitrocellulose of a viscosity reduced by autoclave treatment to a flow rate of about 15–25 seconds measured by preparing a 10 percent nitrocellulose solution in a mixture of butanol, butylacetate and toluene in the ratio of 3:4:5 and by determining its viscosity in a Cochius-viscosimeter (7 mm.) at 18 centigrade.

4. The method according to claim 1, wherein the evaporation of the water contained in the mixture of nitrocellulose and polyhydric alcohol having a water content of at least 18 percent, is effected during the dissolving process at a rate which corresponds to the rate of the nitrocellulose gelatinization.

5. The method according to claim 1, wherein the proportion of the nitro compounds: the mixture of nitrocellulose and nitrated polyhydric alcohol is chosen from 1:1 to 3:2.

6. The method according to claim 1, wherein the propellant formed from the molten mixture is cooled to a temperature of about 25° C. which is maintained during the solidifying process of the mass.

7. The method according to claim 1, wherein the production of the melt is effected under partial vacuum and while stirring, so as to eliminate air bubbles.

8. The method according to claim 1, wherein the mixture of nitrocellulose and polyhydric alcohol is introduced into the molten nitro compound while maintaining therein a temperature from about 10° C. to 20° C. above the melting point of the nitro compound.

9. The method according to claim 1, wherein the temperature of the solution is increased by approximately 10 centigrade after the elimination of the water for a short period sufficient for completely eliminating air bubbles from the molten mass.

10. The method according to claim 1, wherein the molten mixture is cooled down below its solidification temperature and is shaped in this under-cooled state.

11. The method according to claim 1, wherein the molten mass is shaped shortly before solidification is quite completed, the shaping being terminated at room temperature.

12. The method according to claim 1, wherein the shaped and solidified powder units are allowed to stand at room temperature for a few minutes.

References Cited in the file of this patent

UNITED STATES PATENTS

1,783,372	Woodbury	Dec. 2, 1930
1,867,283	Stettbacher	July 12, 1932
2,247,392	Lindsley	July 1, 1941
2,384,730	Davis et al.	Sept. 11, 1945