Patented Apr. 19, 1932 1,854,776

UNITED STATES PATENT OFFICE

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NITROCELLULOSE PROPELLENT POWDER

No Drawing. Application filed February 13, 1931. Serial No. 515,642.

This invention relates to nitrocellulose propellent powder having certain advantageous properties, and to a process of making such powder.

This application is a continuation as to common subject matter of my copending application Serial No. 81,086, filed January 13, 1926.

The object of my invention is to produce a smokeless propellent powder from nitrocellulose without the aid of nitroglycerine which will possess greatly reduced hygroscopic qualities as compared with a powder made from nitrocellulose only. A further object of my invention is the elimination of the white luminous flash such as is produced at the muzzle of guns by the present pyro service powder of the United States Government. This white luminous muzzle flash is commonly attributed to the ignition of the combustible gases formed during the combustion of smokeless powder, due to their high temperature when emerging from the muzzle of the gun and coming in contact with the oxygen of the air. The gaseous products formed by the combustion of smokeless powder are nitrogen, carbon dioxide, carbon monoxide, hydrogen, water vapor and small amounts of methane. Of these the combustible gases are carbon monoxide, hydrogen and methane. The white luminous flash at the muzzle of the gun is due to the combustion of these latter gases in the presence of oxygen. This combustion can be prevented in the case of small arms by firing into an atmosphere of carbon dioxide. When the white luminous flash is eliminated in this manner, or is eliminated by the use of a powder containing suitable ingredients, only a small reddish glow appears at the muzzle of the gun upon firing. This glow is not readily visible and can be easily concealed.

A further object of my invention is the production of a nitrocellulose propellent powder which, besides being of greatly reduced hygroscopicity and flashless in most guns, contains no water soluble ingredients aside from the volatile solvents, ether and ethyl alcohol, which may be used in the manufacture, and therefore can be dried not only in air but also in hot water to more effectively and expeditiously remove the volatile solvents added for the purpose of assisting in the colloiding of the nitrocellulose.

The hygroscopicity of a nitrocellulose propellent powder is a factor largely of the amount, and nitrogen content, of the nitrocellulose used. For example, nitrocellulose of 12.60% nitrogen content will contain about 2.00% moisture when in equilibrium with 70% relative humidity at 30° C. A nitrocellulose of 13.15% nitrogen will contain about 1.5% moisture under the same conditions. Colloiding the nitrocellulose with ether and alcohol has but little effect on the hygroscopicity of the nitrocellulose in the small rifle powder grains and even in powder grains suitable for the 75 m/m field gun, but there is a gradual reduction in hygroscopicity as the size of the powder grains is increased or, in other words, as the amount of residual solvent ether and alcohol left in the powder is increased.

I have found that certain classes of organic compounds are particularly suitable for the double purpose of reducing the hygroscopicity of the nitrocellulose and eliminating the luminous white muzzle flash at the same time. The compounds which I have found especially suitable are dibutylphthalate, diethylphthalate, dibutyltartrate, ethyl palmitate, acetyllaurins, etc. These compounds possess the desirable properties of being good solvents for nitrocellulose, liquid at ordinary temperature, of relatively low volatility, especially when colloided with nitrocellulose; besides being substantially insoluble in water and substantially non-hygroscopic. These

compounds are further characterized by being deterrent materials of a non-explosive character, containing a relatively small percentage of oxygen and a relatively high percentage of carbon and hydrogen.

I have further found that the quantity of the above compounds required to eliminate the muzzle flash of a nitrocellulose propellant is relatively small, so that when used alone with nitrocellulose the quantity required to produce flashlessness, particularly in the smaller guns, would be insufficient to have much effect on reducing the hygroscopicity of the nitrocellulose.

I have further discovered that in order to produce a nitrocellulose propellent powder which will have greatly reduced hygroscopicity as compared with, for example, the present pyro powder of the United States Government and at the same time be flashless in many guns, it is desirable to substitute for a portion of the nitrocellulose, in addition to the portion substituted by the flash eliminating compound, a substantially non-hygroscopic and water insoluble nitro-aromatic compound which when liquid has a substantial solvent action on the nitrocellulose.

As an example of a nitro-aromatic compound which answers my purpose I may mention dinitrotoluene. While ordinary 1-2-4 dinitrotoluene is a solid and as such has no water-proofing action on the nitrocellulose, I subject the powder composition containing dinitrotoluene, at some stage of its manufacture, to a temperature sufficient in the presence of a flash reducing ingredient such as dibutylphthalate to cause the mixture to melt. As both dinitrotoluene and dibutylphthalate, either alone or in mixture, are excellent solvents for nitrocellulose, there is obtained a thorough colloiding of the nitrocellulose by the mixture, resulting in a substantial reduction in the hygroscopicity of the nitrocellulose. This reduction is greater than the reduction due to simply substituting a portion of the nitrocellulose by an equal portion of the above ingredients, and is due to a depression of the hygroscopic qualities of the nitrocellulose by the colloiding action of the mixture of non-volatile solvents.

My invention may therefore be said to comprise, as one important feature, the combination of a nitro-aromatic compound with a flash eliminating compound, both of which are substantially water insoluble and non-hygroscopic and both of which are substantial solvents, alone or in admixture, for nitrocellulose. The substitution of a substantial portion of nitrocellulose by these two ingredients, in addition to the so-called water-proofing effect of the ingredients themselves on the nitrocellulose, produces a nitrocellulose propellent powder of greatly reduced hygroscopicity and flashless in many guns.

I do not wish to be understood as asserting that propellent powders made in accordance with my invention are non-hygroscopic, as it has been my experience that all powders, whether of the nitrocellulose or of the nitroglycerine type, possess a definite degree of hygroscopicity. Furthermore, the hygroscopicities of propellent powders made in accordance with my invention are very much lower than those of the usual type of nitrocellulose powders. As proof of the above I present the following hygroscopic tests made by exposing powders of the compositions as shown to a relative humidity of 70% at a temperature of 30° C. until equilibrium was reached.

	Composition, exclusive of stabilizer			Mean web	Percentage moisture in equilibrium with 70% relative humidity at 30° C.
	Nitrocellulose of 13.15% N.	Dinitrotoluene	Dibutylphthalate		
				Inches	
1	100%	None.	None.	0.0234	1.25%
2	95%	None.	5%	.0218	0.98%
3	90%	None.	10%	.0217	0.81%
4	85%	None.	15%	.0222	0.66%
5	80%	None.	20%	.0230	0.59%
6	95%	5%	None.	.0214	0.96%
7	90%	10%	None.	.0221	0.84%
8	85%	15%	None.	.0228	0.73%
9	80%	20%	None.	.0220	0.64%
10	90%	5%	5%	.0216	0.75%
11	85%	10%	5%	.0226	0.66%
12	80%	10%	10%	.0231	0.60%
13	100% pyro of 12.60% N	None.	None.	.0225	1.80%

In the above table the compositions disclosed in lines 1 to 10 and 12 to 13 are not made in accordance with my invention. The composition in line 11, however, is illustrative of my new composition.

The moisture content of the powders was determined by heating for six hours in vacuo at 50–60° C. to prevent loss other than moisture.

Thus by a combination of 10 parts dinitrotoluene and 5 parts dibutylphthalate with 85 parts nitrocellulose, I obtain the same hygroscopicity as given by 15 parts of either of these ingredients with 85 parts nitrocellulose without the disadvantage of using 15 parts of either ingredient.

The same advantage as regards hygroscopicity and elimination of flash may be obtained by substituting for the dibutylphthalate many other deterrent non-volatile solvents for nitrocellulose.

To illustrate this point I give the results of ballistic test in the 75 m/m field gun model of 1897 using the 13½ pound projectile of powders of various compositions, together with the results of hygroscopic tests at 70% relative humidity at 30° C.:

Composition [1]			Weight of charge	Muzzle velocity	Mean pressure	Hygroscopicity 70% relative humidity at 30° C.[2]	Luminous white muzzle flash
Nitrocellulose of 13.15% nitrogen	Dinitrotoluene or substitute	Flash eliminating ingredient					
			Ounces	*Feet per second*	*Lbs. per sq. inch*		
85%	10% DNT	5% dibutylphthalate	28	1956	35950	0.77%	None
85%	10% DNT	5% dimethyldiphenylurea	27¾	1945	35810	0.78%	None
85%	10% DNT	5% acetyl laurins	28¾	1947	32280	0.76%	None
85%	10% DNT	5% ethyl palmitate	30	1949	30600	0.82%	None
85%	10% DNT	5% diethylphthalate	27¾	1949	33510	0.69%	None
85%	10% DNT	5% dibutyltartrate	27	1925	31900	0.70%	None
85%	10% trinitrotoluene	5% dibutylphthalate	27	1952	35770	0.76%	None

[1] 1% added diphenylamine as a stabilizer.
[2] Moisture determined by heating 6 hours in vacuum oven at 50–60° C.

In place of dimethyldiphenylurea, diethyldiphenylurea or methylethyl-diphenylurea may be used.

With the exception of the dimethyldiphenylurea, diethyldiphenylurea and methylethyldiphenylurea, all of the above flash eliminating ingredients are liquid. They are also excellent solvents for nitrocellulose. While tetra substituted urea compounds are solid, when mixed with the dinitrotoluene mixtures can be obtained melting below 80° C. that is, at a temperature well within suitable limits for safe manufacture, especially when the powder is subjected to water drying treatment after the removal of volatile solvents. It should, therefore, be understood that either or both the nitro-aromatic compound and the flash eliminating ingredient may be solid provided that a mixture of the two will melt below a temperature of about 80° C. and thus colloid the nitrocellulose by reason of their combined solvent action on the same.

I have found that no single composition will give flashless results in all types of guns. In some guns, due to relatively short barrel and relatively severe ballistic requirements, it is often impossible to obtain flashless results with a powder which may give flashless results in some other gun. Furthermore, that the manner in which the powder is ignited, the quantity and arrangement of the supplementary black powder ignition charge are all of great importance in some guns in connection with obtaining flashless results. I have further found that in some guns the type of powder grain is of importance, and that the strip type of powder grain appears to give better results in some guns than the multi- or single perforated.

I have further found that the chemical stability of powder made in accordance with my invention, for example from nitrocellulose, dinitrotoluene, dibutylphthalate and diphenylamine, is far greater than that of powder made from nitrocellulose and diphenylamine only; this I attribute as being due to the thorough colloiding of the nitrocellulose by the mixture of dinitrotoluene and dibutylphthalate used and the solution of the diphenylamine in the latter mixture.

Nitrocellulose of relatively high nitrogen is preferred in order to obtain the advantage of the lower hygroscopicity possessed by nitrocellulose of high nitrogen content. I no not limit myself to the use of nitrocellulose with a nitrogen content of 13.15% which has been previously set forth in certain examples as purely illustrative. It will be apparent from the foregoing that I can use nitrocellulose of much higher nitrogen content, for example as high as 13.50, or even higher, and in conjunction therewith increased or decreased amounts of dinitrotoluene and dibutylphthalate depending on the ballistic and chemical qualities desired and whether or not flashless results are desired. I, therefore, do not limit myself as regards the maximum nitrogen content of the nitrocellulose. It will also be apparent that I can use nitrocellulose of lower nitrogen content than 13.15% with various amounts of dinitrotoluene and dibutylphthalate, but as nitrocellulose of lower nitrogen content is more hygroscopic and of less potential than nitrocellulose of higher nitrogen content, I prefer to use nitrocellulose with nitrogen content in excess of 12.85%. As indicated in the foregoing, I can use nitrocellulose having a nitrogen content greater than 13.50, but heretofore nitrations other than by laboratory methods have not produced a product having satisfactory stability.

While I may use more than 10% of the nitro-aromatic compound, such as dinitrotoluene, in the composition, I have found that this amount is very satisfactory to give with nitrocellulose of about 13.15% nitrogen content and 2–5% of dibutylphthalate, a propellent powder possessing requisite potential for present type of ordnance. When as much as 5% of dibutylphthalate is used, no muzzle flash is obtained in many of the smaller guns. For example, flashless results are obtained with a powder of the composition 85 parts nitrocellulose of about 13.15% nitrogen, 10 parts dinitrotoluol, 5 parts dibutylphthalate and 1% diphenylamine when fired in the 75 mm. French field gun model 1897, with the 13½ pound projectile at the usual muzzle

velocity of 1955 feet per second. For this particular gun and projectile the amount of dibutylphthalate may be reduced to 4 parts, the nitrocellulose content being increased to 86 parts and flashless results still be obtained. However, it is preferable to use 5 parts of dibutylphthalate when flashless results are desired in this gun because of providing greater margin of safety as regards flashlessness.

In some guns flashless results may be obtained by increasing the amount of dibutylphthalate as illustrated by the following compositions:

Nitrocellulose of high nitrogen content	Dinitrotoluene	Dibutylphthalate	Diphenylamine
85 parts	10 parts	7 parts	1 part
82 parts	10 parts	8 parts	1 part
80 parts	10 parts	10 parts	1 part

However, the use of too much dibutylphthalate gives rise to an excessive amount of black smoke due to deficient potential and incomplete combustion of the powder.

I have further found that powders containing only 2 to 3 per cent of dibuylphthalate with 10–15% of dinitrotoluene and the balance nitrocellulose plus stabilizer possess to a marked degree the desirable properties such as satisfactory ballistics, improved chemical stability, reduced hygroscopicity as possessed by powder made of the composition 85 parts nitrocellulose, of 13.15% nitrogen content, 10 parts dinitrotoluene, 5 parts dibutylphthalate and 1 part diphenylamine and are preferred for use in a number of guns where flashless results are either not desired or where flashlessness is a secondary conideration to other properties. For example, a powder of the composition 87 parts of nitrocellulose of 13.15% nitrogen, 10 parts dinitrotoluene, 3 parts of dibutylphthalate and 1 part of diphenylamine gives very satisfactory ballistic results in the larger guns, particularly on account of slightly increased potential and is also entirely suitable for use in smaller guns where flashlessness is not desired, although in some of the smaller guns this composition gives flashless results.

The manufacture of the powder requires no special skill. The nitrocellulose is dehydrated with denatured ethyl alcohol of suitable grade and then colloided in a suitable mixer with the addition of ether. There is added in the ether or directly to the mixer, the dinitrotoluene and the dibutylphthalate. Due to the solvent action of the latter two ingredients, the amount of ether and alcohol required is somewhat less than usually used for nitrocellulose powders not containing these ingredients. Acetone may be used to replace all or part of the ether. Diphenylamine is usually added as a stabilizer and is usually dissolved in the ether. The colloid may be pressed either in cylindrical grains with one or more perforations or without perforations, or in the ribbon or strip form of grain or any other kind.

The grains of powder are given thorough solvent recovery treatment before the final drying, which may be in air or in hot water or a combination of both at a temperature not in excess of 60° C., although a higher temperature may be used without injury to the chemical stability of the powder.

As many apparetnly widely different embodiments of this invention may be made without departing from the spirit thereof, it is to be understood that I do not limit myself to the foregoing examples or descriptions except as indicated in the following patent claims:

I claim:

1. A propellent powder, capable of being water dried, comprising nitrocellulose incorporated with a deterrent explosive and a flash-eliminant ingredient, each of which when in liquid form has a substantial solvent action on the nitrocellulose the deterrent explosive being present in greater amount than the flash-eliminant ingredient.

2. A propellent powder, capable of being water dried, comprising nitrocellulose incorporated with a nitro-aromatic compound and a flash-eliminant ingredient, each of which when in liquid form has a substantial solvent action on the nitrocellulose the deterrent explosive being present in greater amount than the flash-eliminant ingredient.

3. A propellent powder, capable of being water dried, comprising nitrocellulose incorporated with a nitro-aromatic compound and a flash-eliminant ingredient, each of which when in liquid form has a substantial solvent action on the nitrocellulose, and each of which is substantially insoluble in water, the deterrent explosive being present in greater amount than the flash-eliminant ingredient.

4. A propellent powder, capable of being water dried, containing nitrocellulose, a polynitrotoluene, and a dialkyl phthalate.

5. A propellent powder, capable of being water dried, comprising nitrocellulose, an organic nitro-compound other than nitrocellulose which is substantially non-hygroscopic and water-insoluble and which when in liquid form has a substantial solvent action on nitrocellulose, and an alkyl ester of an organic acid, said ester having flash-eliminating properties and being further characterized by having in liquid form a substantial solvent action on nitrocellulose, a low volatility when colloided with nitrocellulose, and by being substantially insoluble in water, and substantially non-hygroscopic.

6. A propellent powder, capable of being water dried, comprising nitrocellulose having incorporated therein a nitro-aromatic compound, and a flash-eliminant ingredi-

ent, the nitroaromatic compound and the flash-eliminating ingredient being of such character that a mixture of the two is liquid at a temperature below 80° C., and in this liquid condition capable of colloiding nitrocellulose, the nitro-aromatic compound being present in greater amount than the flash-eliminant ingredient.

7. A propellent powder, capable of being water dried, containing nitrocellulose, dinitrotoluene, and a member of a group consisting of dibutyl phthalate, diethyl phthalate, dibutyl tartrate, ethyl palmitate, and acetyl-laurin, as a flash-eliminant.

8. A propellent powder, capable of being water dried, containing nitrocellulose, dinitrotoluene and dibutyl phthalate.

9. A propellent powder, capable of being water dried, containing nitrocellulose, dinitrotoluene, dibutyl phthalate and diphenylamine.

10. A nitrocellulose propellent powder, the hygroscopicity of which is depressed below that of the nitrocellulose itself by a mixture incorporated therein of a nitro-aromatic compound and a flash-eliminant ingredient, both of which when liquid have substantial solvent action on the nitrocellulose, the nitro-aromatic compound being present in greater amount than the flash-eliminant ingredient.

11. A propellent powder as defined in claim 1 in which at least a substantial part of the nitrocellulose has a nitrogen content of 12.85 per cent to 13.50 per cent.

12. A propellent powder as defined in claim 2 in which at least a substantial part of the nitrocellulose has a nitrogen content of 12.85 per cent to 13.50 per cent.

13. A propellent powder as defined in claim 3 in which at least a substantial part of the nitrocellulose has a nitrogen content of 12.85 per cent to 13.50 per cent.

14. A propellent powder as defined in claim 4 in which at least a substantial part of the nitrocellulose has a nitrogen content of 12.85 per cent to 13.50 per cent.

15. A propellent powder as defined in claim 5 in which at least a substantial part of the nitrocellulose has a nitrogen content of 12.85 per cent to 13.50 per cent.

16. A propellent powder as defined in claim 6 in which at least a substantial part of the nitrocellulose has a nitrogen content of 12.85 per cent to 13.50 per cent.

17. A propellent powder capable of being water dried, containing nitrocellulose, in combination with a flash eliminant taken from a group consisting of dibutyl phthalate, diethyl phthalate, dibutyl tartrate, ethyl palmitate, and acetyl-laurin, in which at least a substantial part of the nitrocellulose has a nitrogen content of 12.85 per cent to 13.50 per cent.

18. A propellent powder as defined in claim 1 in which at least a substantial part of the nitrocellulose has a nitrogen content of from 13.05 per cent to 13.25 per cent.

19. A propellent powder as defined in claim 2 in which at least a substantial part of the nitrocellulose has a nitrogen content of from 13.05 per cent to 13.25 per cent.

20. A propellent powder as defined in claim 3 in which at least a substantial part of the nitrocellulose has a nitrogen content of from 13.05 to 13.25 per cent.

21. A propellent powder as defined in claim 4 in which at lease a substantial part of the nitrocellulose has a nitrogen content of from 13.05 to 13.25 per cent.

22. A propellent powder as defined in claim 5 in which at least a substantial part of the nitrocellulose has a nitrogen content of from 13.05 to 13.25 per cent.

23. A propellent powder as defined in claim 6 in which at least a substantial part of the nitrocellulose has a nitrogen content of from 13.05 to 13.25 per cent.

24. A propellent powder as defined in claim 1 in which at least a substantial part of the nitrocellulose has a nitrogen content greater than 12.85 per cent.

25. A propellent powder as defined in claim 2 in which at least a substantial part of the nitrocellulose has a nitrogen content greater than 12.85 per cent.

26. A propellent powder as defined in claim 3 in which at least a substantial part of the nitrocellulose has a nitrogen content greater than 12.85 per cent.

27. A propellent powder as defined in claim 4 in which as least a substantial part of the nitrocellulose has a nitrogen content greater than 12.85 per cent.

28. A propellent powder as defined in claim 5 in which at least a substantial part of the nitrocellulose has a nitrogen content greater than 12.85 per cent.

29. A propellent powder as defined in claim 6 in which at least a substantial part of the nitrocellulose has a nitrogen content greater than 12.85 per cent.

30. A propellent powder capable of being water dried, containing nitrocellulose, in combination with a flash eliminant taken from a group consisting of dibutyl phthalate, diethyl phthalate, dibutyl tartrate, ethyl palmitate, and acetyl-laurin, in which at least a substantial part of the nitrocellulose has a nitrogen content of from 12.85 per cent to 13.35 per cent.

31. A propellent powder capable of being water dried, containing nitrocellulose, incorporated with a flash eliminant taken from a group consisting of dimethyldiphenylurea, diethyldiphenylurea, and methylethyldiphenylurea.

32. A propellent powder, capable of being water dried, containing nitrocellulose, having incorporated therein dinitrotoluene, and a member of a group consisting of dimethyl-

diphenylurea, diethyldiphenylurea and methylethyldiphenylurea, as a flash eliminant, the dinitrotoluene being present in greater quantity than the flash-eliminant ingredient.

33. A propellent powder capable of being water dried, containing nitrocellulose, having incorporated therein dinitrotoluene, and a flash-eliminant taken from a group consisting of dimethyldiphenylurea, diethyldiphenylnrea and methylethyldiphenylurea, in which at least a substantial part of the nitrocellulose has a nitrogen content of 12.85 per cent to 13.50 per cent, the dinitrotoluene being present in greater qauntity than the flash-eliminant ingredient.

34. A propellent powder capable of being water dried, containing nitrocellulose, having incorporated therein dinitrotoluene, and a flash-eliminant taken from a group consisting of dimethyldiphenylurea, diethyldiphenylurea and methylethyldiphenylurea, in which at least a substantial part of the nitrocellulose has a nitrogen content of 13.05 per cent to 13.25 per cent, the dinitrotoluene being present in greater quantity than the flash-eliminant ingredient.

35. A propellent powder capable of being water dried, containing nitrocellulose, having incoporated therein dinitrotoluene, and a flash-eliminant taken from a group consisting of dimethyldiphenylurea, diethyldiphenylurea and methylethyldiphenylurea, in which at least a substantial part of the nitrocellulose has a nitrogen content greater than 12.85 per cent, the dinitrotoluene being present in greater quantity than the flash-eliminant ingredient.

36. A nitrocellulose propellent powder containing nitrocellulose, dinitrotoluene and dibutylphalate, and having a hygroscopicity at a relative humidity of 70 per cent and at a temperature of 30° C. below 1 per cent.

In testimony whereof, I affix my signature.

RICHARD GEORGE WOODBRIDGE.