

# UNITED STATES PATENT OFFICE

2,155,499

## METHOD OF WATERPROOFING HYGROSCOPIC MATERIALS

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No Drawing. Application March 23, 1935,  
Serial No. 12,647

12 Claims. (Cl. 52—19)

The present invention relates to a new and improved method of waterproofing materials which are adversely affected by water, and more particularly to a method of waterproofing explosive compositions containing water-soluble salts, as well as to the products obtained by such method of treatment.

The use of hygroscopic ingredients in compositions which tend to be adversely affected by moisture or water is frequently necessary when a non-hygroscopic equivalent is not readily available. Where such conditions prevail, it is essential to protect the composition from moisture by some suitable means. This is sometimes accomplished by incasing the product in a water-impervious wrapper or jacket. An alternative procedure consists in coating the individual particles of the hygroscopic material with a waterproofing agent such as a mineral or vegetable oil, a fat, a wax or the like.

As heretofore carried out, the waterproofing has generally been accomplished by applying the agent in a liquid condition to the individual particles of the hygroscopic material. The results of such procedure, however, were not altogether satisfactory. Thus it was frequently found that, if sufficient oil were employed to waterproof the material, the physical and chemical properties of the coated material were markedly and adversely affected. This was particularly noticeable in waterproofing the water-soluble ingredients of commercial dynamites, for example ammonium nitrate, sodium nitrate, and the like.

As is well known, waterproofing the ammonium nitrate by means of oily materials such as liquid petrolatum diminishes the sensitiveness of the dynamite to propagation by detonation. Moreover, these materials are not entirely effective in imparting water resistance, unless employed in amounts so large that the coated material has an excessive oxygen deficiency, which is very undesirable under many conditions.

Various attempts have been made to bring about this waterproofing effect by a more satisfactory method. For example, lycopodium, starch, and other light powdery materials have been suggested as waterproofing agents. Again, S. G. Baker, in copending application No. 719,299, filed April 6, 1934, discloses for this purpose an improved waterproofing agent consisting of the metallic salts of high molecular weight fatty acids.

An object of my invention is an improved process for rendering impervious to water materials which are adversely affected by moisture. A fur-

ther object is a water-soluble material so treated with a suitable composition as to be water-resistant. A still further object is an explosive composition containing a hygroscopic ingredient, the water resistance of which has been substantially improved without adversely affecting the explosive properties thereof. Other objects will become apparent as my invention is hereinafter fully described.

I have found that the foregoing objects are accomplished provided the material which is adversely affected by water or moisture is treated at ordinary temperatures with resinous mixed esters of a polyhydric alcohol, a polycarboxylic acid, and a fatty acid of at least six carbon atoms.

The resinous mixed esters mentioned in the foregoing comprise indefinite polymeric molecules which are prepared by methods well known in the synthetic resin art, either by reacting the polyhydric alcohol, polycarboxylic acid and fatty acid simultaneously; or by first heating together the polyhydric alcohol and a polyhydric alcohol ester of the fatty acid, adding the polycarboxylic acid, and heating to resinification. In the preparation of these resinous mixed esters, polyhydric alcohols such as glycerin, glycol, diethylene glycol, pentaerythritol, p-xylene glycol, mannitol, monoethylin, monobenzylin, and the like may be employed. Likewise any resinifying polycarboxylic acid such as succinic, adipic, sebacic, malic, maleic, citric, phthalic, diphenic, naphthalic, and the like may be used. The fatty acid may be caproic, capric, lauric, myristic, palmitic, oleic, stearic, arachidic, hydroxystearic, undecylenic, ricinoleic, coconut oil acids, soya bean oil acids, linseed oil acids, and the like. For the sake of convenience, I shall hereinafter refer to the resins defined in this paragraph as "resinous mixed esters".

The "resinous mixed esters" generally are applicable according to my invention, but I prefer to employ a "resinous mixed ester" derived from glycerin, phthalic acid and either stearic, oleic, or palmitic acid. In particular I find that resinous mixed esters of glycerin, phthalic acid and stearic acid are especially effective waterproofing materials, and these are the preferred embodiments of my invention.

My invention is generally applicable to materials which are adversely affected by water or moisture. It may be employed, for example, with sodium chlorate, the hygroscopicity of which is objectionable for many purposes, as in chlorate explosive compositions. Again, it may be employed in waterproofing sodium nitrate, as used,

for example, in black powder. It may be employed also to prevent the setting of any material which becomes caked or hardened by the absorption of moisture or water. I find it highly advantageous, for example, for protecting ammonium nitrate from setting by the absorption of moisture.

In order to describe my invention more clearly, I shall cite a number of typical examples in which a resinous mixed ester of glycerin, phthalic acid and stearic acid is employed. This is done by way of illustration only, and is not to be regarded as a limitation, since it is apparent that any of the substances within the purview of this invention may be used in substantially the same manner with beneficial results.

As a typical example of the application of my invention to a single water-soluble substance, the waterproofing of ammonium nitrate may be given as illustrative. This is achieved simply by rumbling the ammonium nitrate for a short time with one-half of one per cent. of its weight of a resinous mixed ester of glycerin, phthalic acid and stearic acid. The individual particles of the ammonium nitrate are thereby coated with a very thin film of the solid resin, which greatly increases the resistance to water or moisture. Preferably the coating is carried out at a temperature of 150-160° F., which is above the melting point of the coating compound. It will now be apparent from the foregoing disclosure of my invention that any similar water-soluble or hygroscopic material such as sodium chlorate, sodium nitrate, sodium chloride, ammonium phosphate and the like may be treated in a similar fashion with similar beneficial results.

My invention may also be used in waterproofing a complex composition, as for example, an ammonia dynamite. Here also as little as one-half of one per cent of the resinous mixed ester of glycerin, phthalic acid and stearic acid is sufficient to improve the water resistance very markedly. As illustrative of the improved effect, the following examples are given, in which (1) represents a dynamite in which a resinous mixed ester of glycerin, phthalic acid and stearic acid is present, and (2) represents a similar dynamite which contains no waterproofing material:

	(1)	(2)
	Percent	Percent
Nitroglycerin.....	14.0	14.0
Ammonium nitrate.....	35.0	35.0
Sodium nitrate.....	36.8	37.0
Glyceryl phthalate-stearate resin.....	0.5	-----
Wood pulp.....	1.0	1.0
Starch.....	5.7	6.0
Sulfur.....	6.0	6.0
Chalk.....	1.0	1.0
	100.0	100.0

The ingredients may be incorporated in the usual manner, or the ammonium nitrate and sodium nitrate may be coated with the waterproofing ingredient as in the previous example, before incorporation in the dynamite composition. Preferably, however, I use the latter procedure.

The excellent waterproofing effect of the invention is strikingly illustrated by the fact that a dynamite composition, formulated according to my invention such as that designated (1) above, has a water resistance of 16 hours, while a similar composition (2), not so formulated, has a water resistance of only ¼ hour. The water resistance value represents the maximum time in hours during which cartridges of the various

dynamites were submerged in water, at the end of which no failures to detonate in four trials were obtained, the detonation being brought about by a commercial blasting cap.

It is apparent that other compositions such as black powder, cement, or any mixture containing hygroscopic or water-soluble materials, or which tends to become set from the effect of water, may be made water-impervious by the application of my invention. This may be accomplished either by coating the particular hygroscopic ingredients with one of the materials according to my invention, before incorporation in the composition, or the waterproofing material may be added to the composition at the time of mixing of the various ingredients. I prefer to coat the hygroscopic materials first, since it is unnecessary to coat the other ingredients in the composition.

My invention may be of advantage, for example, in preventing excess leaching of potassium compounds from fertilizers. Either the potassium salt itself, or the entire fertilizer composition may be made water-resistant according to my invention in the above described manner. By this means, the fertilizer gives up its soluble salts slowly.

Another example of the use of my invention is to be found in integrally waterproofed cement, wherein the sand and cement are incorporated at the time of mixing with a small amount of resinous mixed ester of glycerin, phthalic acid and stearic acid, for example. This material tends to prevent the filling of the interstices between the cement particles with water, with the resulting expansion of the material.

In the application of my invention, various amounts of my new waterproofing materials may be employed. Preferably, however, I use amounts from 0.1 to 2.0% by weight of the total composition, although 0.5% is ordinarily quite satisfactory.

In the foregoing detailed description of my invention, it is apparent that many variations can be made without departing from the spirit or scope of the invention. I therefore intend to be limited only in accordance with the following patent claims.

I claim:

1. An explosive composition comprising an ingredient imparting water-resistant properties to the water-soluble materials thereof by being present as a water protective coating thereon, said ingredient consisting of a resinous mixed ester of a polyhydric alcohol, a polycarboxylic acid and a fatty acid of at least six carbon atoms.

2. A black powder composition containing an ingredient imparting water-resistant properties to the water-soluble materials thereof, said ingredient comprising a resinous mixed ester of a polyhydric alcohol, a polycarboxylic acid and a fatty acid of at least six carbon atoms.

3. A dynamite composition comprising an explosive nitric ester and a water-soluble inorganic salt, said salt having as a water-protecting coat at least one resinous mixed ester of a polyhydric alcohol, a polycarboxylic acid and a fatty acid of at least six carbon atoms.

4. A dynamite composition according to claim 3, in which the nitric ester comprises nitroglycerin and the water-soluble salt comprises ammonium nitrate.

5. A dynamite composition comprising nitroglycerin, ammonium nitrate and from 0.1 to 2.0% by weight of a resinous mixed ester of glycerin,

phthalic acid and stearic acid said ester forming a water protective coat for said ammonium nitrate.

5 6. A composition of matter for use in explosive charges comprising a granular water soluble material normally having a tendency to cake on standing, and incorporated therewith to form a water protective coating thereon, a resinous mixed ester of a polyhydric alcohol, a polycarboxylic acid and a fatty acid of at least six carbon atoms.

10 7. A composition of matter for use in explosive charges comprising ammonium nitrate and incorporated therewith to form a water protective coating thereon, a resinous mixed ester of a polyhydric alcohol, a polycarboxylic acid and a fatty acid of at least six carbon atoms.

15 8. An explosive composition comprising ammonium nitrate and an ingredient imparting water resistance to said ammonium nitrate by being present as a water protective coating thereon, said ingredient consisting of a resinous mixed ester of a polyhydric alcohol, a polycarboxylic acid and a fatty acid of at least six carbon atoms.

20 9. A composition of matter comprising sodium

chlorate and incorporated therewith an ingredient imparting water-resistant properties thereto, said ingredient consisting of a resinous mixed ester of a polyhydric alcohol, a polycarboxylic acid and a fatty acid of at least six carbon atoms.

5 10. A composition of matter comprising sodium nitrate and incorporated therewith an ingredient imparting water-resistant properties thereto, said ingredient consisting of a resinous mixed ester of a polyhydric alcohol, a polycarboxylic acid and a fatty acid of at least six carbon atoms.

10 11. The method of rendering water-resistant, a material comprising sodium chlorate, which comprises incorporating with said material at least one resinous mixed ester of a polyhydric alcohol, a polycarboxylic acid and a fatty acid of at least six carbon atoms.

15 12. The method of rendering water-resistant, a material comprising sodium nitrate, which comprises incorporating with said material at least one resinous mixed ester of a polyhydric alcohol, a polycarboxylic acid and a fatty acid of at least six carbon atoms.

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