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LOW DENSITY CELLULOSE MATERIALS

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This invention relates to improvements in low-density cellulose materials, and more particularly to an improved low density product adapted for use as an absorbent ingredient of explosives, for example, those of the types containing a liquid high explosive ingredient. The present application constitutes a continuation of an application filed by the present applicant December 9, 1935, and bearing Serial No. 53,598.

An object of the invention is attained in the production of a low-density cellulose material such as will enable meeting the demand for bulky low density permissible powders such as are employed in the mining industry. This type of explosive must in nearly all cases be of the type known as Ammonia Permissibles, in the production of which it has become well nigh impossible with existing bulking or absorbent materials, to obtain the low density desired by the trade, without sacrificing strength, sensitivity and powder fume classification.

In keeping with the foregoing demand, the present invention has as an important object, the attainment of a bulking or absorbent material which will enable the production of explosives of the stated class, as well as those of other types, without any sacrifice in strength and sensitivity, and resulting in a distinct improvement in the fume classification, i. e., a gas resulting from explosive combustion which is characterized by a substantially lower volume and proportion of noxious gases than is the case with heretofore existing explosives of this type, employing other bulking ingredients.

In keeping with the foregoing, it is a major objective of the present invention to improve the fume classification of certain explosives of existing types, by reduction of the carbon monoxide content of the fume.

Yet another object of the invention is attained in an ability, through compounding the improved absorbent material of the present invention with other ingredients, to employ a higher proportion of ammonium nitrate as well as increased amounts of liquid explosive such as nitroglycerin, so as to produce, for any given density of explosive, a stronger and more sensitive product.

Yet another object of the invention is to meet in an improved manner, the existing demand for explosive cartridges of standard size, but of such bulk as will provide a maximum number of cartridges per case of given weight; accordingly the present objective may be stated as realized by an explosive characterized by a substantially lower weight standard cartridge, and hence a greater

number of cartridges or units per standard case.

Yet another object of the invention is attained in an improved pulverulent cellulose absorbent or bulking material having a lower density than heretofore prevailing products for comparable purposes, and which, in spite of an extremely low weight, does not undergo any material impairment of form, shape or bulk of its particles on wetting by liquids, for example, the liquid explosive ingredients characterizing certain types of dynamites.

The foregoing and numerous other objects will clearly appear from the following detailed description of the materials and processes characterizing the present invention.

The novel ingredient principally characterizing the present invention either as utilized of itself, or as mixed or compounded with other ingredients, consists of a cellulose material of extremely light weight. Whatever be the form in which this is supplied to the trade, the manner of its incorporation into soundproofing items and construction materials such as wallboard, as well as the other manifold constructional and industrial uses, will be apparent to those skilled in the several arts to which they pertain.

After numerous and exhaustive experiments with a variety of materials primarily cellulose in nature, I have discovered that the pith of many of the plants of the family Malvaceae, popularly known as the mallow family, produces upon suitable treatment to be described, a pulp or meal which is admirably suited for the purpose noted. The plant family Malvaceae embraces three sub-families usually designated as Malva, Althea and Lavatera, all characterized by a stalk containing a spongy or porous pith, which upon a cleaning and purifying treatment, produces a cellulose material capable of being comminuted to produce either a pulp or a meal of almost feathery characteristics and substantially lower in density than such products as bagasse, balsa wood and products heretofore used for the purposes noted. I have found the plants of the genus *Hibiscus* to be particularly suited for the purpose described, and of the plants of this genus, *Hibiscus militaris*, popularly known as the halberd leaved rose mallow, or wild hollyhock; also suitable and of equal preference, is the *Hibiscus lasiocarpus*. I have also found that all of the plants of the genus *Hibiscus*, being those of the mallow family, possess a distinctive and characteristic pith structure which may be best described as relatively grainless, and almost microscopically skeletonized, and being susceptible of easy optical distinction,

particularly upon slight magnification, over any of the other so-called light weight absorbent or bulking materials heretofore used in the production of high explosive compositions. In addition to the several species heretofore enumerated, there have also been found suitable for the purpose of production of the cellulose bulking material or absorbent of the present invention, the several species of Hibiscus known as *coccineus*, *moscheutos*, *oculiroseus*, *incanus*, *diversifolius*, *aculeatus* and *grandiflorus*. The foregoing is of course not intended as an exhaustive enumeration of species of the genus Hibiscus, nor of those suitable for the purpose of preparation of the improved absorbent material. The species noted, in addition to all of the herbaceous perennials of the family, these being preferred for the present purpose, have, however, been found to contain a desirable pith structure in comparatively pure form, and to possess the characteristic cellular structure of the Hibiscus.

In addition it is to be understood that many of the hybrid varieties derived from plants of the Hibiscus family, are suitable for the noted purpose. An example of such a hybrid is a modification of *Hibiscus lasiocarpus*, being a plant derived from this species and found presently in the State of California, hence referred to, at least locally, as *Hibiscus Californicus*. It is of course obvious that any two species can be crossed, and a hybrid formed therefrom. It is accordingly to be understood that any such hybrid derived directly or indirectly from the known species, will, so long as it possesses the characteristic mallow pith structure, be suitable for the present purpose. It is further to be noted that, although all of the several species enumerated are known botanically, so far as has been revealed by exhaustive plant study and research, no member of the mallow family has heretofore been known in the trade or industry, for any use whatsoever. Accordingly it is distinctly within the scope of the present invention to include any prepared and comminuted cellulosic material derived from the pith of the mallow family, which material has been produced in reasonable quantities by this applicant, and packaged for distribution and sale.

In the recovery of the pulp, it is preferred that the stalks of the plant be cut and allowed to dry, following which the bark and more fibrous portions of the stalk are readily removable as by employing known mechanical decorticating processes. The inner portions of the stalk, comprising principally the heart or pulp, may then be ground in a mill, for example, one of a type ordinarily used to prepare ivory meal, gypsum and similar substances, the grinding being carried to a fineness approximating 20 mesh, and the resulting ground product treated with 1% NaOH solution. Following this treatment the pulp is thoroughly washed with water, following which it is treated with HCl of low concentration, for example, a 1% solution, after which it is washed and thoroughly dried. It is entirely possible to separate the pith and fiber by utilizing water alone, in which case the material may be ground to pass a 20 mesh screen, repeatedly washed with water until a good separation is obtained. Although satisfactory and economically feasible, depending upon water costs, the water treatment usually requires slightly more time, and offers a little advantage over the treatment first described, utilizing NaOH and HCl. It will be noted that, in lieu of the treatment by NaOH,

soda ash has been found to give substantially the same results, affording an excellent separation and a considerable saving of time and water.

As illustrating one possible use of the product of my invention in an explosive composition, the following is noted as a preference for the production of a low density dynamite;

	Per cent
Nitroglycerin.....	13.5
Ammonium nitrate.....	58.0
Mallow pulp.....	18.0
Sodium nitrate.....	9.5
Chalk.....	1.0

An explosive produced in accordance with the foregoing, will provide the following results when packed in the form of a cartridge 1¼" by 8", which, for convenience of reference herein, may be referred to as a standard cartridge:

Cartridge weight.....grams..	79.5
Cartridge count.....sticks per case..	285
Sensitivity.....inches..	6
Rate of detonation.....ft./sec..	5340

The powder is easily packed into a firm stick, which shows after a substantial period of time, no evidence of shrinkage. As providing a basis of comparison of densities, it may here be noted that two well known widely distributed products of comparable formula, except for a different absorbent or cellulose ingredient, average respectively 219 and 250 cartridges or sticks per case.

In a consideration of explosives of the type herein discussed by way of example, the approximate practical limits for the use of the mallow pulp characterizing the present invention, are substantially as appear in the following tables indicating, respectively, lower and upper limits in the proportion of this ingredient:

Nitroglycerin.....	10.0	14.5
Sodium nitrate.....	13.0	4.5
Ammonium nitrate.....	75.0	55.5
Mallow pulp.....	1.0	25.0
Chalk.....	1.0	1.0

For purposes of providing a single tabulation ascribing practical limits in an explosive of the type under discussion, the following is given:

	Per cent
Nitroglycerin.....	5-15
Ammonium nitrate.....	40-85
Sodium nitrate.....	0-20
Sodium chloride.....	0-20
Mallow pulp.....	1-25

As indicative of the density range afforded by the foregoing formulae, standard size (1¼" x 8") cartridges of the explosives may be produced therefrom within a range of weights of 75 grams to 145 grams.

It will be understood, however, that in explosives or other compositions of matter in which a higher percentage or proportion of cellulose or a cellulose absorbent is customarily employed, the permissible percentage of such material may substantially exceed the highest figure given for the novel product of the present invention. Such limits are to be understood only as being those prescribed by reasons of reaction, flame propagation, optimum explosive mixtures, etc., but that no limits need be ascribed, up to and including 100%, for any physical reason. Otherwise expressed, the mallow pulp material characterizing the present invention may be utilized with or

without added ingredients, depending upon the intended purpose.

In the preparation of the novel material such as mallow pith meal, an average density of the comminuted pith meal has been noted as substantially less than .1 gram, this figure often attaining a value as low as .076 gram, and varying up to .094 gram. The figures here given represent the approximate weight in grams of 1 cc. of the material under discussion, based on a determination under 25 lbs. pressure. Among the more suitable low density materials heretofore employed for the purposes primarily anticipated for the present, there may be mentioned bagasse pith, derived by crushing and cleaning spent sugar-cane, and straining it to remove the long fibers. Other known modes of treatment follow, but after the treating process there results a product which rarely ever exhibits a lower density than .148, from which it will appear that the novel product of the present invention offers marked advantages in the production of an extremely bulky or low density product, whether used alone, or compounded or admixed with other ingredients.

Many advantages accrue from the use of the bulking materials here described, even though it be not desired to utilize the material in a form having its lowest density. Otherwise expressed, in case there is desired a material having the advantageous physical characteristics of the products disclosed, the mixtures thereof may be readily controlled in density without necessarily varying the proportion of mallow pulp. This is possible since the ground material may be varied in density between limits of the order of .076 for the pure carefully cleaned and ground pith, to .213-.215, the latter figures representing the approximate density of the bark alone as cleaned and prepared from *Hibiscus militaris* or *Hibiscus lasiocarpus*. It will be obvious to those skilled in the art, whether the material is utilized in explosives or otherwise, that any desired density of the absorbent or cellulose ingredient may be obtained between the limits mentioned, merely by varying the mixture of materials derived respectively from the bark and from the pith.

It is an important feature and result arising out of the use of the absorbent material herein described, that it permits of the production of explosive compositions in which the total carbonaceous material is relatively less, and the oxygen-carrying salts are substantially greater, for an explosive of a given density, than is the case with any existing explosive composition of comparable type heretofore known in the trade. It results from this fact that the combustion on explosion produces a relatively high volume of carbon dioxide and a relatively lower volume of carbon monoxide, the latter being the principal noxious gas upon which the Bureau of Mines classifications are based. For reasons arising out of the ability to use my new bulking or absorbent material, it becomes possible for the first time to employ a higher proportion of ammonium nitrate, for example, as well as a higher proportion of nitroglycerin, than in comparable explosives of heretofore existing types, in any given density. Consequently, it is possible to produce for a given density, a stronger and more sensitive explosive than possible with any heretofore known absorbent material, all of which are, as understood, of considerably higher density than the mallow pulp hereinabove referred to and described.

By way of illustration of the improvements attained in a reduction of the volume and proportion of noxious gases in the fume, the following results are presented as typifying the improvements attained by the use of mallow pith in place of bagasse, the latter having been selected for comparison as being one of the lowest density absorbents in prevalent use in explosives of comparable type:

Ingredients	A	B	C
Nitroglycerin.....	15.00	15.00	15.00
Ammonium nitrate.....	55.50	55.00	60.00
Sodium nitrate.....	10.00	10.00	11.00
Bagasse.....	16.50	15.00	
Mallow pith.....			12.00
Starch.....	1.00	4.00	1.00
Chalk.....	1.00	1.00	1.00

Volume of poisonous gases formed by 680 grams of each:

	Liters
A.....	87.85
B.....	120.69
C.....	54.24

In the above tabulation, sample A represents a standard product heretofore produced by the manufacturer of the explosive within the present invention, while sample B is a well-known product of comparable density offered by a competing manufacturer, and sample C is essentially the same as sample A except for slight adjustments due to substitution of the mallow pith for the bagasse heretofore employed. It is apparent from a comparison of the above results, that by the use of mallow pith as an absorbent it is possible for the first time to produce a lower density explosive than those heretofore prevalently offered to the trade or otherwise known to this applicant, and at the same time attain a product in which the volume of poisonous gases formed upon combustion, is materially lower than in the case of prevailing, comparable explosives.

In order to enable a comparison of the three samples A, B and C supra, on a basis of their fume analyses, the following is presented to show the relative percentage volumes of the different gaseous ingredients resulting from combustion:

Analysis of gases

	A	B	C
Carbon dioxide.....	21.56	16.94	25.51
Oxygen.....			
Carbon monoxide.....	21.07	25.75	15.41
Hydrogen.....	29.66	34.96	23.12
Methane.....	.65	.94	1.20
Nitrogen.....	27.06	21.41	34.76
Hydrogen sulphide.....	100.00	100.00	100.00

From the foregoing it will appear that while explosives of heretofore prevalent and standard type and designated as "Ammonia Permissibles", show about equal volumes, in the fume, of CO₂ and CO in one instance, and in another a materially greater proportion of CO than of CO₂, the explosive formed in accordance with the present invention is characterized by a fume analysis in which the CO is substantially three-fifths of the volume of CO₂, and in any case, distinctly less than three-fourths of the volume of CO₂. From this it becomes evident that an improved result is presented to the art, in this material reduction in proportion of noxious gases. It may be noted that no H₂S was found in any of the

fume analyses of the three samples above scheduled.

5 Since the present description is merely illustrative and not to be regarded as limiting, it is to be understood that the process employed in preparing the raw material and in its recovery from its natural sources, may be varied substantially, as may be the type of explosive or other substance in or with which the low density cellulose product may be incorporated or utilized, all 10 without departing from the intended scope of the claims hereunto appended.

I claim as my invention:

15 1. A bulking material adapted as an absorbent for use in explosives, and consisting essentially of cellulose, and including in substantial part, the purified and ground pith of a plant of the family Malvaceae.

20 2. As an article of manufacture, cellulose bulking material adapted for use in explosive compositions, and composed essentially of the washed and comminuted pith of a plant of the genus Hibiscus.

25 3. An explosive composition characterized by low density and including nitroglycerin, ammonium nitrate, and an absorbent for said nitroglycerin present in an amount between limits of substantially 1% and 25%, the absorbent consisting, at least in substantial part, of washed and comminuted pulp of a plant of the mallow 30 family.

4. A low density dynamite consisting of nitroglycerin in a proportion substantially within the range of 10% to 15%, nitrates substantially with-

in the range of 55% to 70%, a small amount of an inert ingredient, and a cellulose absorbent material substantially within the range of 10% to 25%, the last said material being formed essentially of cleaned and comminuted pith from 5 a plant of the mallow family.

5. A high explosive including nitroglycerin substantially 10%, ammonium nitrate substantially 75%, sodium compounds substantially 13%, a small amount of an inert mineral ingredient together with a cellulose absorbent comprising 10 the pith of a plant of the mallow family, the composition being of such a density that a standard cartridge thereof weighs not substantially in excess of 145 grams.

15 6. A high explosive composition including nitroglycerin substantially 14-15%, ammonium nitrate substantially 55-56%, sodium compounds in an amount of the order of 4-5%, a small amount of an inert mineral ingredient, together 20 with a cellulose absorbent sufficient to make up the remainder and substantially 24-26%, the greater portion of the absorbent comprising the pith of a mallow plant, and the composition being of such density that a standard cartridge thereof has a weight substantially within the 25 range of 75 to 100 grams.

7. An explosive composition comprising a liquid explosive nitric ester and mallow pith.

8. An explosive comprising a liquid explosive 30 nitric ester, nitrates and mallow pith.

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