

## CHAPTER VI

### SMOKELESS POWDER

An account of smokeless powder is, in its main outlines, an account of the various means which have been used to regulate the temperature and the rate of the burning of nitrocellulose. After the degree of nitration of the nitrocellulose, other factors which influence the character of the powder are the state of aggregation of the nitrocellulose, whether colloided or in shreds, the size and shape of the powder grains, and the nature of the materials other than nitrocellulose which enter into its composition.

#### Bulk Powder

The first successful smokeless powder appears to have been made by Captain Schultze of the Prussian Artillery in 1864. At first he seems only to have impregnated little grains of wood with potassium nitrate, but afterwards he purified the wood by washing, boiling, and bleaching, then nitrated it, purified the nitrated product by a method similar to that which had been used by von Lenk, and finally impregnated the grains with potassium nitrate alone or with a mixture of that salt and barium nitrate.<sup>1</sup> The physical structure of the wood and the fact that it contained material which was not cellulose both tended to make the nitrated product burn more slowly than guncotton. The added nitrates further reduced the rate of burning, but Schultze's powder was still too rapid for use in rifles. It found immediate favor for use in shot guns. It was manufactured in Austria by a firm which in 1870 and 1871 took out patents covering the partial gelatinization of the powder by treatment with a mixture of ether and alcohol. The improved powder was manufactured between 1872 and 1875 under the name of *Collodin*, but the Austrian gov-

<sup>1</sup> Brit. Pat. 900 (1864).

ernment stopped its manufacture on the grounds that it infringed the government's gunpowder monopoly. A company was formed in England in 1868 to exploit Schultze's invention, a factory was established at Eyeworth in the New Forest in 1869, and the

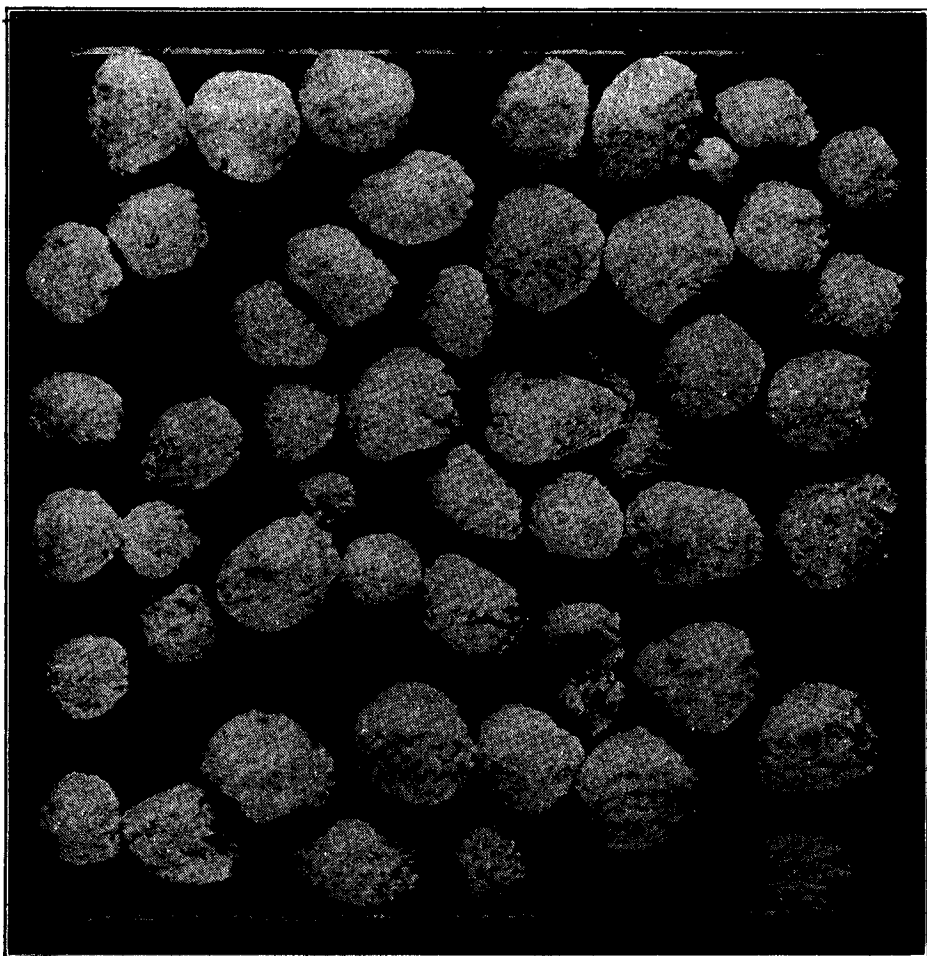


FIGURE 70. Shreddy Grains of Bulk Powder (25 $\times$ ). (Courtesy Western Cartridge Company.)

methods of manufacture were later improved by Griffiths and achieved great success. In 1883 Schultze entered into a partnership in Germany and started a factory at Hetzbach in Hesse-Darmstadt.

The next successful smokeless powder was invented<sup>2</sup> at the works of the Explosives Company at Stowmarket in England. It

<sup>2</sup> Brit. Pat. 619 (1882) to Walter F. Reid and D. Johnson.

was called E. C. powder (Explosives Company), and consisted of nitrocotton mixed with potassium and barium nitrates with the addition of coloring matter and small amounts of other organic material. It was made into grains which were hardened by being partially gelatinized with ether-alcohol. A separate company was organized to develop the invention, and the manufacture was started at Green Street Green, near Dartford, in Kent.

Schultze powder and E. C. powder are known as *bulk sporting* powders, either because they are loaded by bulk or because, for the same bulk, they have about the same power as black powder. Bulk powders burn quickly. They are used in shot guns, in hand grenades, in blank cartridges, and occasionally in the igniter charges which set fire to the dense colloided propellant powder which is used in artillery.

Bulk powders are made in considerable variety, but they consist always of nitrocellulose fibers which are stuck together but are not completely colloided. Some contain little else but nitrocellulose; others contain, in addition to potassium and barium nitrates, camphor, vaseline, paraffin, lampblack, starch, dextrine, potassium dichromate or other oxidizing or deterrent salts, and diphenylamine for stabilization, and are colored in a variety of brilliant hues by means of coal-tar dyes. In the United States bulk powders are manufactured by one or the other of two processes, either one of which, however, may be modified considerably; the materials are incorporated under wooden wheels, grained, and partially gelatinized, or the grains are formed in a still where a water suspension of pulped nitrocellulose is stirred and heated with a second liquid, a solvent for nitrocellulose which is volatile and immiscible with water.

Three typical bulk powders are made up according to the approximate formulas tabulated below. The nitrogen content of

Nitrocellulose .....	84.0	87.0	89.0
% N in nitrocellulose .....	13.15	12.90	12.90
Potassium nitrate .....	7.5	6.0	6.0
Barium nitrate .....	7.5	2.0	3.0
Starch .....	.....	.....	1.0
Paraffin oil .....	.....	4.0	.....
Diphenylamine .....	1.0	1.0	1.0

the nitrocellulose is an average secured by mixing pyrocellulose and guncotton. A batch usually amounts to 200 pounds, 100

pounds of water is added and about 90 grams of rosaniline or some other, generally bright-colored, water-soluble dyestuff, and the charge is incorporated by milling for about 45 minutes in a wheel mill which is built like a black-powder mill but is smaller and has light wooden wheels. The charge is then run through a mechanical rubber, which consists of wooden blocks rubbing with a reciprocating motion on a perforated zinc plate; the larger lumps are broken up and the material is put into proper condition for granulating. For this purpose about 50 pounds is placed in a copper pan or "sweetie barrel" which is revolving in a vat of hot water and is heated by that means. The pan rotates fairly rapidly, say at about 15 r.p.m., and carries the powder up along its sloping side to a point where it is scraped off by suitably arranged wooden scrapers and falls back again. It thus receives a rolling motion which has the effect of granulating the powder into spherical grains. The operation requires about 40 minutes, and its completion is indicated by the failure of the powder to carry up on the pan because of the loss of moisture.

After it has been granulated, the powder is given a preliminary screening with a 12-mesh sieve. The material which is retained on the sieve is returned to the wheel mill. That which passes through is hardened. It is put into a horizontal revolving cylinder and a mixed solvent, consisting of about 1 part of acetone and 6 parts of alcohol, is added in the proportion of 1 gallon of solvent to 15 pounds of powder. Acetone dissolves nitrocellulose, alcohol does not; the mixed solvent swells and softens the fibers and makes them stick together. The cylinder is rotated, while hot air is blown through, until the solvent has been volatilized. During this process the temperature is allowed to rise as high as 50° or 55°. The product, which consists of grains now more or less completely agglutinated, is given a final screening. In a typical case, the portion passed by a 12-mesh sieve and retained by a 50-mesh sieve is taken; it is given a final drying and is ready for use.

In a typical example of the still process for the manufacture of bulk sporting powder, 500 pounds of pulped nitrocellulose (12.60% N) is placed in a vertical cast-iron still along with 700 gallons of water containing 2% of potassium nitrate and 6% of barium nitrate dissolved in it. The material is mixed thoroughly

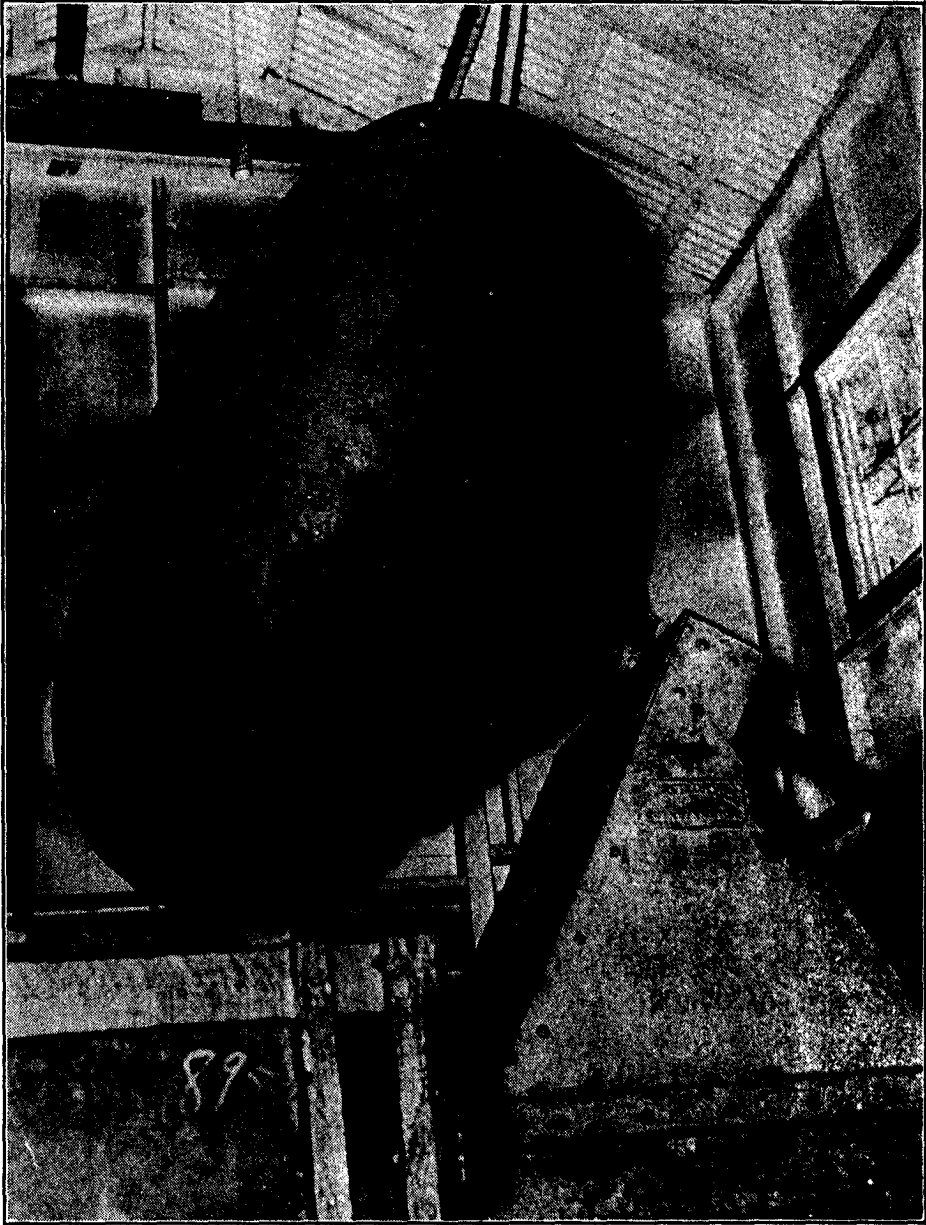


FIGURE 71. Sweetie Barrel. (Courtesy Western Cartridge Company.) The moist and mixed ingredients of bulk powder, tumbled in this apparatus, take on the form of grains. Similar equipment is used for sugar-coating pills and for applying a deterrent coating or a graphite glaze to grains of colloid smokeless powder.

and agitated actively by mechanical stirrers while 145 gallons of mixed solvent (2 parts butyl acetate, 3 parts benzene) containing about 3 pounds of diphenylamine dissolved in it is pumped in. The stirring is violent enough to break the solvent phase up into many small droplets, and around each droplet a globular cluster of nitrocellulose shreds builds up. The mixture is stirred continuously and distilled in vacuum at a temperature of about 30°. The distillate is collected in a separating device in such manner that the solvent is drawn off while the water is returned to the still. At the end of the process the contents of the still consists of water with potassium and barium nitrates in solution along with granules of the wet but otherwise finished powder. The individual grains of the powder are broken apart by a very violent stirring, filtered off in a centrifuge, and dried. The finished powder contains about 1 or 1.5% of potassium nitrate and about 3.5% of barium nitrate.

### Early History of Colloided Powders

1884. The first smokeless powder which was satisfactory for use in rifled guns was the dense, colloided *poudre B*,<sup>3</sup> invented by the French physicist, Paul Vieille, and adopted immediately for the use of the French army and navy. It was made by treating a mixture of soluble and insoluble nitrocotton with ether-alcohol, kneading to form a stiff jelly, rolling into thin sheets, cutting into squares and drying, or, in later practice, extruding through a die in the form of a strip, cutting to length, and drying. The results of the first proof firing of this powder, made with a 65-mm. cannon, were communicated to the Minister of Armaments on December 23, 1884.

It was then established that the new processes would permit the ballistic effect of black powder to be secured with the same pressure and with the charge reduced to about a third, and that the power of the arms could be increased notably, with a slight reduction of the charge, while still keeping to the ordinary pressures. The standard powder for the model 1886 rifle was determined in the early months of the year 1885. . . . The standard powder made possible an increase of velocity of 100 meters per second for the same pressures.

<sup>3</sup> *Poudre blanche*, white powder in contradistinction to *poudre N*, *poudre noire*, black powder.

... This substitution has had the foreseen consequence of suppressing the smoke from the shooting.<sup>4</sup>

The author of the note in the *Mémorial des poudres* in which the above-quoted public announcement was made concerning the new powder was so impressed by the importance of the invention that he concludes the note by saying:

It results from this that the adaptation to firearms of any other explosive known at the present time would be able to bring to the armament only a perfecting of detail, and that a new progress, comparable to that which has been realized recently, cannot be made except by the discovery of explosives of a type entirely different from those which chemistry today puts at our disposition.

French powder for the military rifle consists of small square flakes lightly glazed with graphite. The glazing serves to retard slightly the rate of burning of the surface layer, and, more important, it serves to make the powder electrically conducting and to prevent the accumulation of a static charge during the blending of small lots of the powder into a single, ballistically uniform large lot. For guns the powder consists of unglazed strips. The squares and strips, ignited over their entire surfaces, burn for lengths of time which depend upon their thicknesses, and they retain, during the burning, surfaces which change but little in area until at the end the grains are completely consumed.

1888. The second successful dense smokeless powder was the *ballistite* which was invented by Alfred Nobel.<sup>5</sup> This was a stiff gelatinous mixture of nitroglycerin and soluble nitrocellulose in proportions varying between 1 to 2 and 2 to 1, prepared with the use of a solvent which was later removed and recovered. Nobel appears to have been led to the invention by thinking about celluloid, for the patent specification states that the substitution of almost all the camphor in celluloid by nitroglycerin yields a material which is suitable for use as a propellant. In the method of manufacture first proposed, camphor was dissolved in nitroglycerin, benzene was added, and then dry, pulped, soluble nitrocellulose; the mixture was kneaded, the benzene was allowed to evaporate, and the material was rolled between warm rollers

<sup>4</sup> *Mém. poudres*, 3, 11-12 (1890).

<sup>5</sup> Brit. Pat. 1471 (1888).

to make it completely homogeneous. It was rolled into thin sheets which were cut with a knife or scissors into the desired shape and size. The use of nitrostarch instead of part of the nitrocellulose, and the addition of pulverized chlorate or picrate in various proportions, were also mentioned in the patent.

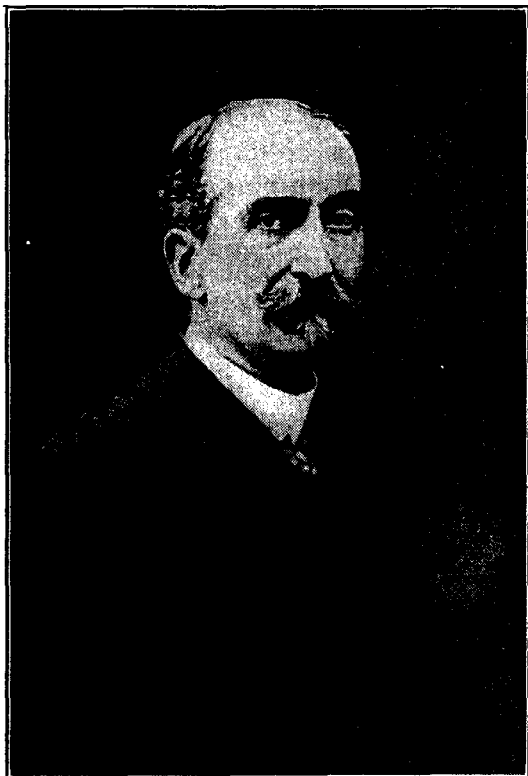


FIGURE 72. Paul Vieille (1854-1934). Inventor of *poudre B*, the first progressive-burning smokeless powder, 1884. Author of classic researches on erosion. Secretary and later, as successor to Berthelot, President of the French Powder and Explosives Commission.

1889. Nobel soon discovered<sup>6</sup> that the use of soluble nitrocellulose made it possible to manufacture ballistite without using camphor or any other solvent. The nitroglycerin and soluble nitrocellulose were brought together under water. As soon as the nitroglycerin had been absorbed by the nitrocellulose, the mass was heated to 80° to complete the gelatinization, and was then rolled and cut up in the usual way. In an alternative process the gelatinization was hastened by using more nitroglycerin than was

<sup>6</sup> Brit. Pat. 9361 (1889).



desired in the powder, and the excess was removed by means of 75% methyl alcohol by which it was extracted while the nitrocellulose was unaffected by that solvent.

1889. Lundholm and Sayers<sup>7</sup> devised a better process of incorporating the materials. The nitroglycerin and the soluble nitrocellulose were brought together under hot water and stirred by means of compressed air. The nitroglycerin presently gelatinized, or dissolved in, the nitrocellulose. The doughlike mass was removed, and passed between rollers heated to 50° or 60° whereby the water was pressed out. The sheet was folded over and passed through the rolls again, and the process was repeated until a uniform colloid resulted. It was rolled to the desired thickness and cut into squares which were generally glazed with graphite and finally blended.

1889. At about the time that Vieille was developing *poudre B*, the British government appointed a committee to investigate and report upon a smokeless powder for the use of the British service. Samples of ballistite and other smokeless powders were procured, the patent specifications relative to them were studied, and the decision was reached to use a powder which differed from Nobel's ballistite in being made from insoluble nitrocellulose containing more nitrogen than the soluble material which he used. The gun-cotton and nitroglycerin were incorporated together by means of acetone, mineral jelly (vaseline) was added, the colloid was pressed through dies into the form of cords of circular or oval cross section, and the acetone was evaporated off. The product was called *cordite*. The experimental work in connection with its development was done mostly in Abel's laboratory, and mostly by Kellner who later succeeded Abel as War Department chemist. Patents<sup>8</sup> in the names of Abel and Dewar, members of the committee, were taken out on behalf of the government in 1889, and later in the same year the manufacture of cordite was commenced at the royal gunpowder factory at Waltham Abbey.

The mineral jelly was added to cordite originally with the idea that it would lubricate the barrel of the gun, but it seems to have no such effect. Actually it is consumed during the combustion. Because of it the powder gases contain a larger number of mols

<sup>7</sup> Brit. Pat. 10,376 (1889).

<sup>8</sup> Brit. Pats. 5614, 11,664 (1889).

at a lower temperature, and produce, with less erosion, substantially the same ballistic effect as the same weight of powder made up without mineral jelly. The original cordite Mk. I. contained guncotton 37%, nitroglycerin 58%, and mineral jelly 5%. This produced such serious erosion of the guns in the British South African war that the composition was modified; the relative amount of nitroglycerin was reduced for the purpose of making it cooler. Cordite M. D. (modified) consists of guncotton 65%, nitroglycerin 30%, and mineral jelly 5%.

Mineral jelly in cordite has a distinct stabilizing action. The material is known to take up nitric oxide in the nitrometer and to cause a falsely low nitrogen analysis if it is present in the material which is being analyzed.<sup>9</sup>

Any distinction between cordite and ballistite which is based upon the methods by which the materials are manufactured is now no longer valid. Certain cordites are made without the use of a volatile solvent. Ballistites are made from soluble and from insoluble nitrocellulose, with and without the use of acetone, ethyl acetate, or other volatile solvent. Cordite is the name of the propellant which is used by the British armed forces. Ballistite, generally in flakes, sometimes in cords and in single-perforated tubes, is the preferred military powder of Italy, Germany, and the Scandinavian countries.

1891. Charles E. Munroe commenced investigations of smokeless powder at the Naval Torpedo Station, Newport, Rhode Island, about 1886, and about 1891 invented *indurite*. This was made from guncotton, freed from lower nitrates by washing with methyl alcohol, and colloidized with nitrobenzene. The colloid was rolled to the desired thickness and cut into squares or strips which were hardened or indurated by the action of hot water or steam. Most of the nitrobenzene was distilled out by this treatment, and the colloid was left as a very hard and tough mass. Indurite was manufactured which gave satisfactory tests in guns ranging in caliber from the one-pounder to the six inch.<sup>10</sup>

1895-1897. After Munroe's resignation from the Torpedo Station, Lieutenant John B. Bernadou, U. S. Navy, took up the

<sup>9</sup> *U. S. Bur. Mines Bull.* 96, "The Analysis of Permissible Explosives," by C. G. Storm, Washington, 1916, p. 44.

<sup>10</sup> Ballistic tests are reported in Munroe's interesting article on "The Development of Smokeless Powder," *J. Am. Chem. Soc.*, 18, 819-846 (1896).

work on smokeless powder and in 1895 patented a powder consisting of a mixture of guncotton, collodion cotton, and potassium nitrate, colloided with acetone, and in 1897 an improved powder made from nitrocellulose alone colloided with ether-alcohol. The nitrocellulose first used contained approximately 12.45% nitrogen, but this was later replaced by pyrocellulose, 12.60% nitrogen. The powder was made in multiperforated cylindrical grains, and was substantially the same as was used by the United States in the first World War. Patents covering various improvements in the manufacture of pyrocellulose powder were taken out in the names of Lieutenant Bernadou and Captain Converse, U. S. Navy, and were licensed or sold to private interests, the United States government retaining the right to manufacture under these patents powder for its own use.

1900–1907. About 1900 the Navy Department built the Naval Powder Factory at Indian Head, Maryland. The plant was capable of producing several thousand pounds of smokeless powder per day, and was enlarged during the course of a few years to a capacity of about 10,000 pounds daily. About 1907 the Ordnance Department, U. S. Army, built at Picatinny Arsenal, Dover, New Jersey, a powder plant with a capacity of several thousand pounds per day.

### Classification of Colloided Nitrocellulose Powders

American pyrocellulose powder and French *poudre B* are *straight nitrocellulose* or *single-base* powders. They are made by the use of a volatile solvent, generally ether-alcohol, which solvent is removed wholly or in large part during the process of manufacture. They are the simplest of colloided powders, the pyrocellulose powder being really the simpler of the two, for it is made from one single kind of nitrocellulose. Modified forms of these powders are made by incorporating into the colloid non-volatile solvents (i.e. solvents which remain in the finished powder) which may be either explosive or non-explosive or by distributing throughout the colloid as a separate phase materials, either explosive or non-explosive, which affect the rate or the temperature of the burning or the strength of the powder. Aromatic nitro compounds, such as DNT, TNX oil, etc., dissolve nitrocellulose or are dissolved by it, and thus constitute themselves non-volatile solvents, but they are also explosives in their

own right, and a nitrocellulose powder which contains one of them might, it would seem, be designated with propriety as a *double-base powder*. This, however, is not in accordance with prevailing usage. The name of double-base powder is reserved for such powders as ballistite and cordite which contain nitrocellulose and nitroglycerin (or perhaps some substitute for nitroglycerin such as nitroglycol). Double-base powders are made both with and without volatile solvent, and are also capable of being modified in all of the ways in which a single base powder may be modified. We have, therefore, colloid powder of various kinds, as follows.

I. Nitrocellulose powder without nitroglycerin

- a. with volatile solvent,
- b. with non-explosive non-volatile solvent,
- c. with explosive non-volatile solvent,
- d. with non-explosive non-volatile non-solvent,
- e. with explosive non-volatile non-solvent.

II. Nitrocellulose powder with nitroglycerin

- a. with volatile solvent,
- b. with non-explosive non-volatile solvent,
- c. with explosive non-volatile solvent,
- d. with non-explosive non-volatile non-solvent,
- e. with explosive non-volatile non-solvent.

III. Coated and laminated powders the grains of which are non-homogeneous combinations of the powders above classified.

This classification is offered, not in any belief that it clarifies a matter which is otherwise difficult to understand, but because it directs attention to the various possibilities and displays their relationships to one another. Some of the possibilities correspond to powders which are or have been used in this country or in Europe, and which are sufficiently described for our present purpose if they are mentioned specifically. Others will be discussed at greater length in the sections, below, which are concerned with the absorption of moisture, with gelatinizing agents, and with flashless charges and flashless powder. All the possibilities are actually exploited, though not always separately.

Cordite MD, it may be noted, is a double base powder made with volatile solvent and containing a non-volatile, non-explosive non-solvent, namely mineral jelly, and is classified in class II *a d*,

while a flashless ballistite of class II *b c* is made by incorporating centralite and DNX oil with nitroglycerin and nitrocellulose, and one of class II *b e* by mixing centralite and nitroguanidine with nitroglycerin and nitrocellulose. The nitroguanidine does not dissolve in the colloid but is distributed through it in a state of fine subdivision. Ten or 15 parts of nitroguanidine incorporated with 90 or 85 parts of pyrocellulose colloided with ether-alcohol gives a mixture which may be extruded through dies and yields a powder (I *a e*) which is flashless. PETN is another substance, insoluble in nitrocellulose colloids, which in the state of a fine powder may be incorporated in single-base or in double-base mixtures to yield powders (I *a e* and II *a e*) which are hotter and more powerful than otherwise.

### Manufacture of Single-Base Powder

The operations in the manufacture of smokeless powder from pyrocellulose, briefly, are as follows.

1. *Dehydrating.* The pulped pyrocellulose contains about 25% moisture when it arrives at the smokeless powder plant. Most of this is squeezed out by pressing with a moderate pressure, say 250 pounds per square inch, for a few moments. The pressure is then released, alcohol in an amount at least equal to the dry weight of the pyrocellulose is forced into the mass by means of a pump, and the pressure is increased to about 3500 pounds per square inch. The process is managed in such fashion that the resulting cylindrical block consists of pyrocellulose moistened with exactly the amount of alcohol which is needed for the formation of the colloid. The requisite amount of ether is added later. The solvent consists altogether of 1 part by weight of alcohol and 2 parts of ether, 105 pounds of the mixed solvent for every 100 pounds of pyrocellulose if the colloid is to be made into 0.30-caliber powder, 100 parts if into powder of which the web thickness is approximately 0.025 inch, and 85 parts for powder having a web thickness of 0.185 inch. The block is received in a cannister of vulcanized fiber and is covered over in order that loss of solvent by evaporation may be reduced to a minimum. From this point on, in fact, the material is kept and is moved from one operation to another in covered cannisters at all times except when it is being worked.

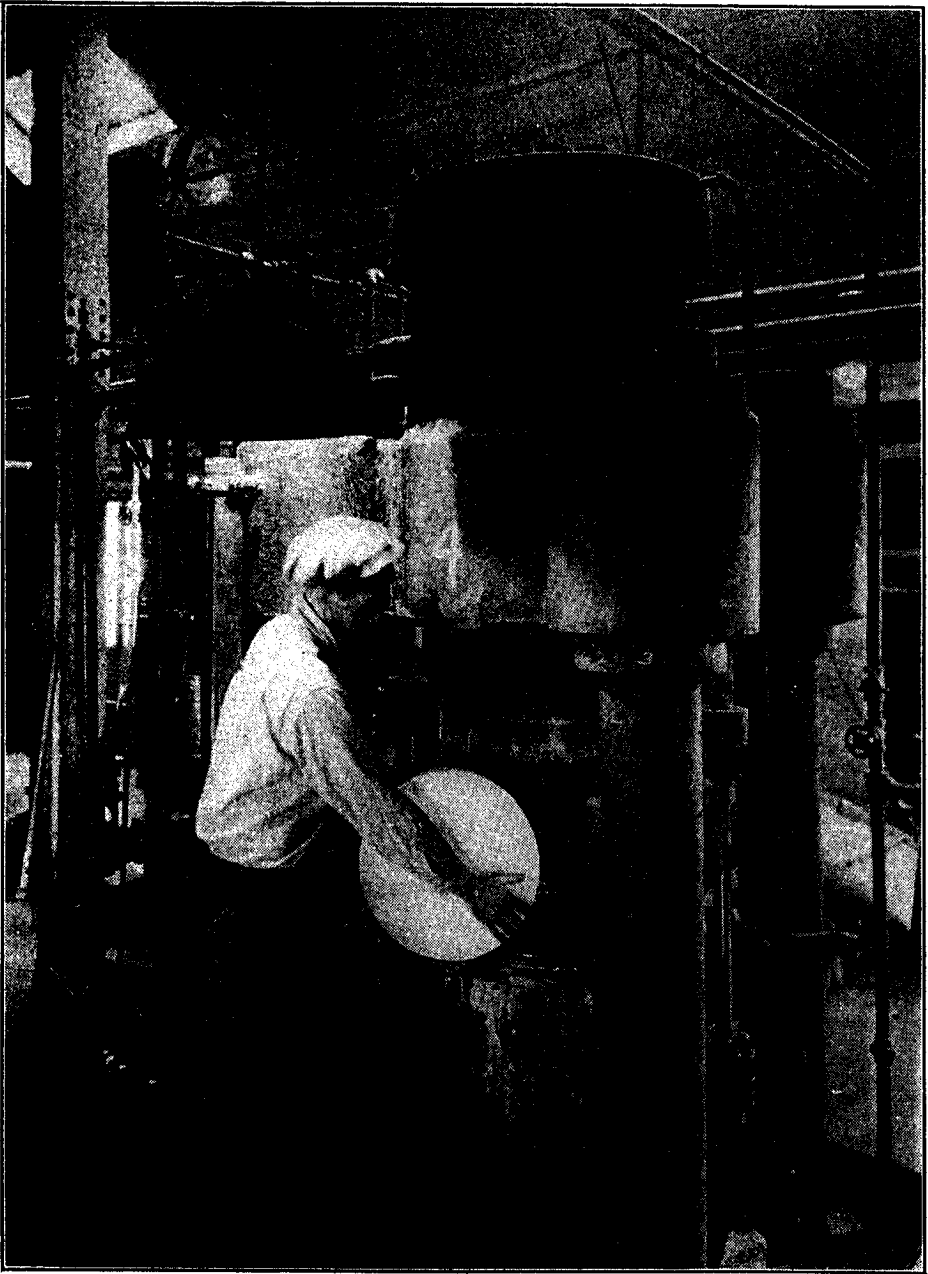


FIGURE 73. Smokeless Powder Manufacture. (Courtesy E. I. du Pont de Nemours and Company, Inc.) Dehydrating Press. The nitrocellulose comes from the dehydrating press in the form of a cylindrical block, impregnated with alcohol, ready for the mixer where ether is added and where it is colloided.

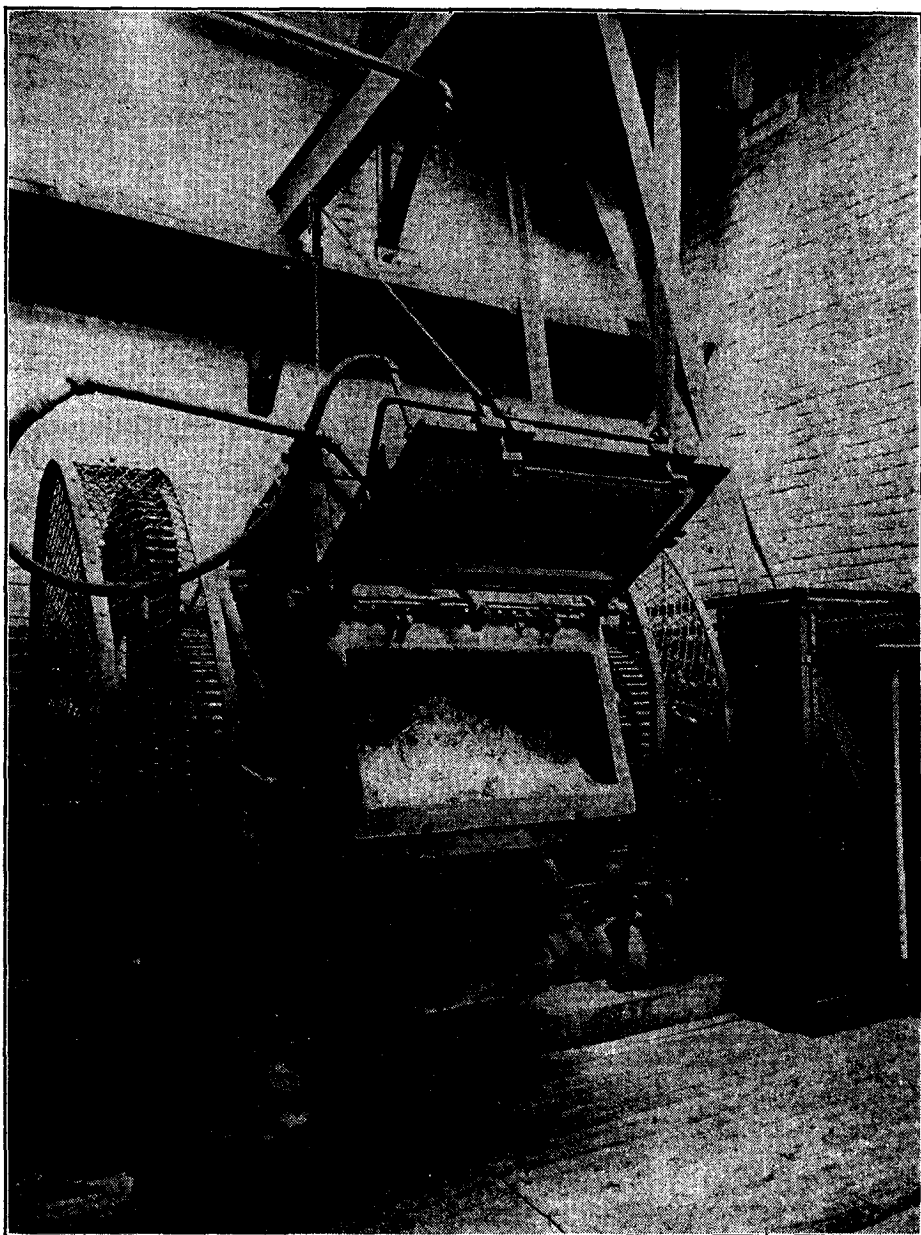


FIGURE 74. Smokeless Powder Manufacture. (Courtesy E. I. du Pont de Nemours and Company, Inc.) Smokeless Powder Mixer—open to show the crumbly, partially colloided material. In use, the apparatus is closed tightly to prevent the loss of volatile solvent.

2. *Mixing or incorporating.* The compressed block from the dehydrating press is broken up by hand against the blades of the mixing machine. This is similar to the bread-mixing machines which are used in large commercial bakeries, and consists of a water-cooled steel box in which two shafts carrying curved blades rotate in opposite directions and effectively knead the material. The ether is added rapidly and mixed in as fast as possible. Diphenylamine sufficient to constitute 0.9–1.1% of the weight of the finished powder is previously dissolved in the ether, and is thus distributed uniformly throughout the colloid. The incorporated material has an appearance similar to that of a mass of brown sugar which has been churned; it is soft enough to be deformed between the fingers, and, when squeezed, welds together in the form of a film or colloid.

3. *Pressing.* The loose and not yet completely colloided material is pressed into a compact cylindrical mass by means of a pressure of about 3500 pounds per square inch in the *preliminary blocking press*. The *preliminary block* is then placed in the *macaroni press* where it is pressed or strained through 1 12-mesh steel plate, 2 sheets of 24-mesh and 1 sheet of 36-mesh steel wire screen, and through the perforations in a heavy plate of brass from which it emerges in wormlike pieces resembling macaroni. A pressure of 3000 to 3500 pounds per square inch is commonly used. The material drops directly into the cylinder of the *final blocking press*, where it is squeezed into a compact cylindrical block of the right size to fit the graining press. A pressure of about 3500 pounds per square inch is maintained for 1 or 2 minutes, and completes the colloidizing of the pyrocellulose. The *final block* is dense, tough, elastic, light brown or amber colored, and translucent.

4. *Graining and cutting.* The colloid is forced by a hydraulic press through dies by which it is formed into single-perforated or into multiperforated tubes. For the formation of a single-perforated tube, the plastic mass is forced in the die into the space which surrounds a centrally fixed steel wire; it is then squeezed past the wire through a circular hole and emerges in the form of a tube. For the formation of a multiperforated tube, 7 such wires are accurately spaced within the die. A pressure of 2500 to 3800 pounds per square inch is used. For small arms powder the head of the press may contain as many as 36 dies, for large-



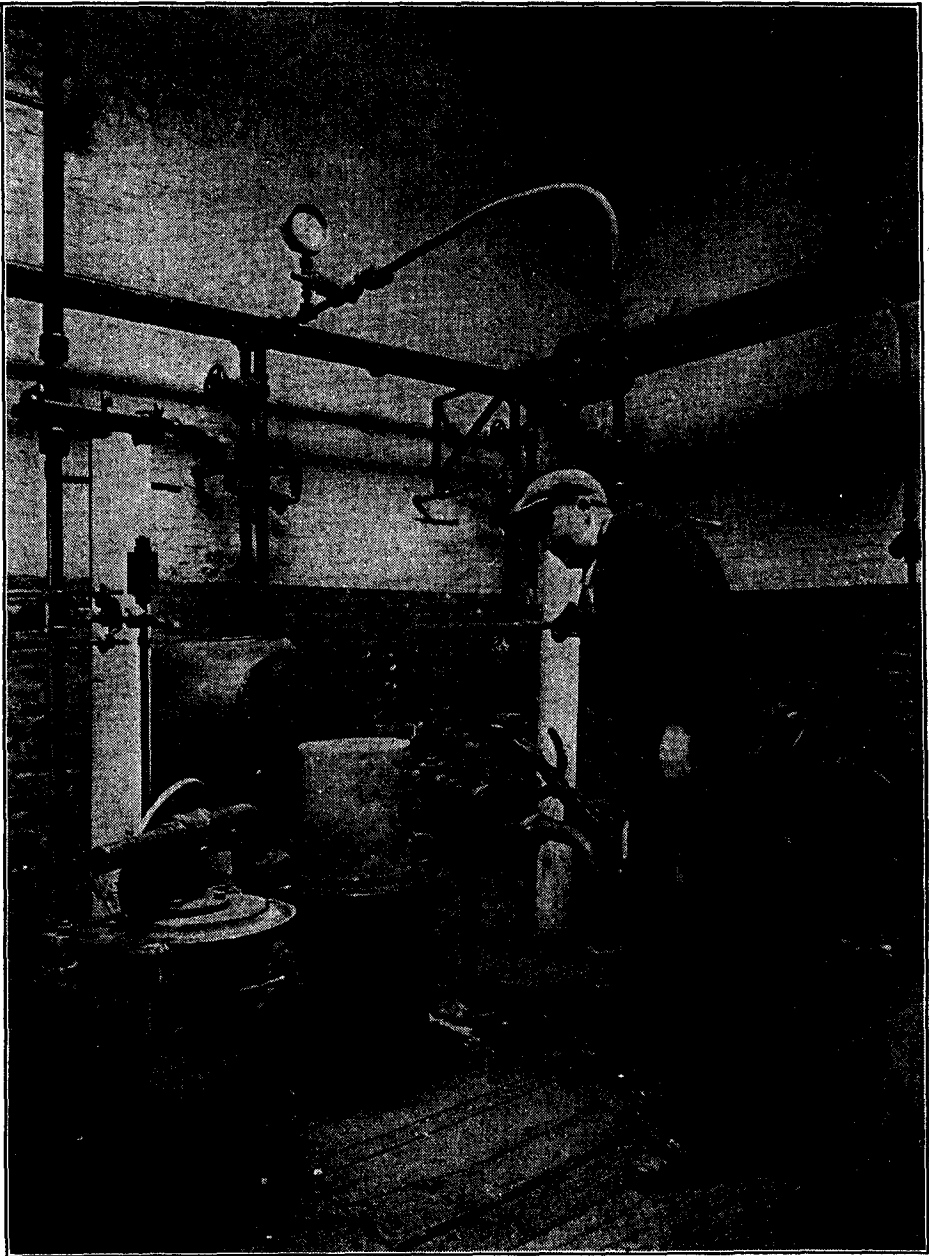


FIGURE 75. Smokeless Powder Manufacture. (Courtesy E. I. du Pont de Nemours and Company, Inc.) Blocking Press.

caliber powder, such as that for the 16-inch gun, it usually contains only one. The cord or rope of powder as it comes from the press is passed over pulleys or through troughs to a rotary cutter where it is cut into short cylinders about 2.1 to 2.5 times as long as their diameters or it is coiled up in a fiber cannister in which it is taken to another room for cutting. In France the colloid is



FIGURE 76. Smokeless Powder Manufacture. (Courtesy E. I. du Pont de Nemours and Company, Inc.) Finishing Press. The colloid is extruded in the form of a perforated cylinder which is later cut into pieces or grains.

pressed through slots from which it emerges in the form of ribbons which are cut into strips of a length convenient for loading into the gun for which the powder is intended.

5. *Solvent recovery.* The *green powder* contains a large amount of ether and alcohol which presents a twofold problem: (1) the recovery of as much of the valuable volatile solvent as is economically feasible, and (2) the removal of the solvent to such an extent that the finished powder will not be disposed either to give off or to take up much volatile matter or moisture under changing atmospheric conditions. For the recovery of the solvent, the pow-

der is put into a closed system and warm air at 55–65° is circulated through it; the air takes up the alcohol and ether from the powder and deposits much of it again when it is passed through a condenser. It is then heated and again passed through the powder. In some European plants the air, after refrigeration, is passed upward through an absorption tower down which cresol or other suitable liquid is trickling. This removes the ether which was not condensed out by the cooling, and the ether is recovered from it by distillation. The whole process of solvent recovery requires careful control, for the colloid on drying tends to form a skin on its surface (the way a pot of glue does when drying) and the skin tends to prevent the escape of volatile matter from the interior of the powder grain.

6. *Water-drying.* Powder is now most commonly dried by the rapid water-drying process whereby the formation of a skin upon its surface is prevented and certain other advantages are gained. Water at 65° is circulated throughout the powder. The water causes the production of microscopic cracks and pores through which the alcohol and ether escape more freely. These substances leave the powder to dissolve in the water, and then the ether in particular evaporates out from the water. When the volatile solvent content of the powder is sufficiently reduced, the powder grains are taken out and the water with which they are superficially covered is removed in a dry-house or in a continuous dryer at 55–65°. The finished powder contains 3.0 to 7.5% of volatile solvent in the interior of the grain, the amount depending upon the thickness of the web, and 0.9 to 1.4% of *external moisture*, mostly water actually resident in the cracks or pores of the surface. The amount of moisture which the powder thus holds upon its surface is an important factor in maintaining its ballistic stability under varying atmospheric conditions. The amount ought to be such that there is no great tendency for the moisture to evaporate off in dry weather, and such also that there is no great tendency for the powder to take up moisture in damp weather. The importance of surface moisture is so considerable that the French powder makers, long before there was any thought of using warm water to dry the powder, were accustomed to submit it to a *trempage* or tempering by immersion in water for several days. Later, periods of air-drying were alternated

with periods of *trempe* in warm water at temperatures sometimes as high as 80°.

Powder for small arms is generally *glazed* with graphite, by which treatment its attitude toward the loss and absorption of moisture is improved, and by which also it is made electrically conducting so that it can be *blended* without danger from static

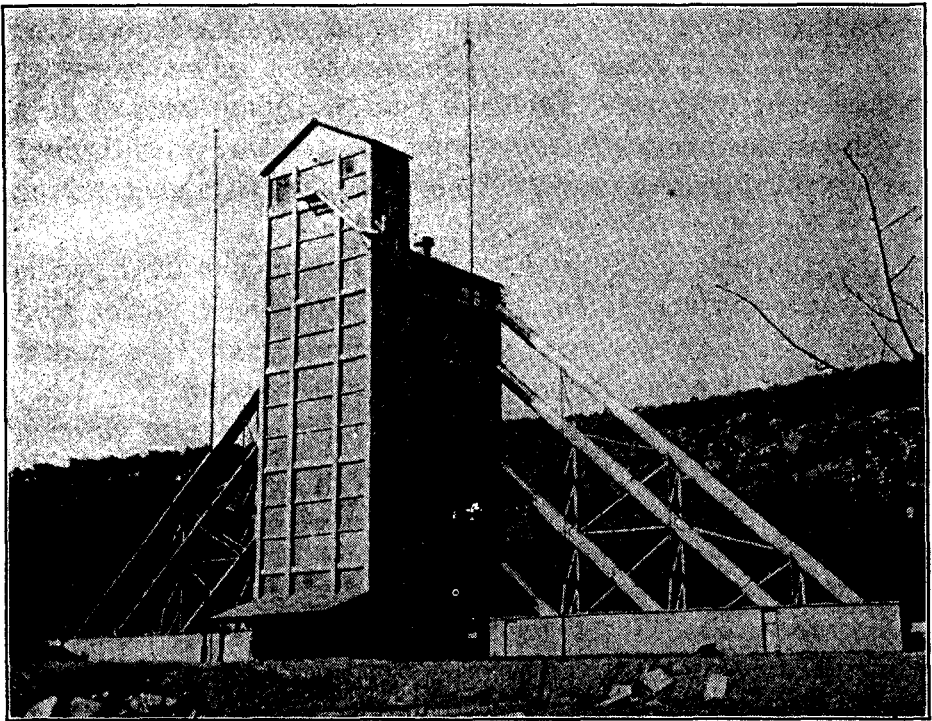


FIGURE 77. Smokeless Powder Blending Tower. The powder is blended by being made to flow through troughs and bins. Lots as large as 50,000 pounds of rifle powder and 125,000 pounds of cannon powder have been blended in this tower.

electricity and loaded satisfactorily by a volumetric method. The powder is blended in order that large lots can be made up which will be ballistically uniform, and hence that the proof firing, the operations of loading, and the calculations of the artilleryman may all be either simplified in kind or reduced in amount. Powder in short cylindrical grains, such as is used in the United States, is particularly easy to blend, but the blending of strips, or of long tubes or cords, is obviously difficult or impracticable. The finished powder is stored and shipped in airtight boxes which contain 110–150 pounds.

## Stabilizers

The spontaneous decomposition of nitrocellulose in the air produces nitrous and nitric acids which promote a further decomposition. If these products however are removed continuously, the uncatalyzed decomposition is extremely slow, and smokeless pow-

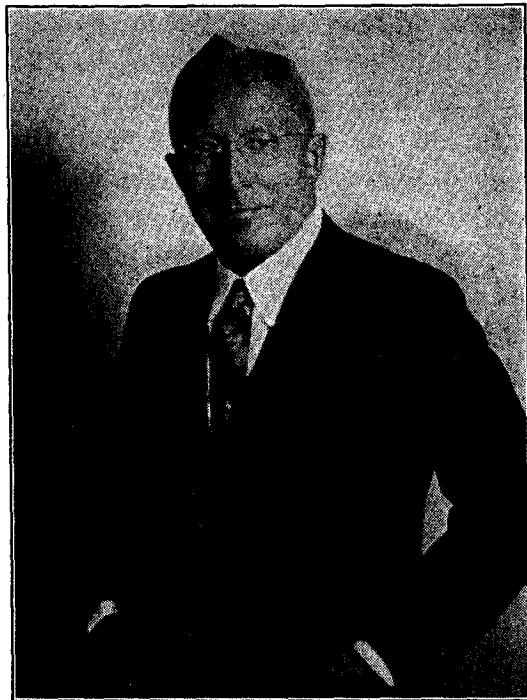


FIGURE 78. Bernhart Troxler. (Greystone Studios, Inc.) Introduced many innovations into the manufacture of smokeless powder and improved the design of equipment in such manner as to increase production while reducing the hazard—the steam-air-dry process for double-base powder, methods of coating, apparatus for solvent recovery, water drying, and air drying of single-base powder without transferring the powder during the three operations. His whole professional life has been devoted to smokeless powder, with the Laflin and Rand Powder Company until 1913, and afterwards with the Hercules Powder Company from the time when that company was organized and built its first smokeless powder line.

der may be stabilized by the addition to it of a substance which reacts with these acids and removes them, provided neither the substance itself nor the products of its reaction with the acids attacks the nitrocellulose.

Vieille suggested the use of amyl alcohol as a stabilizer, and powder containing this material was used in France until 1911

when, in consequence of the disastrous explosion of the battleship *Jena* in 1907 and of the battleship *Liberté* in 1911, both ascribed to the spontaneous inflammation of the powder, and in consequence of the researches of Marqueyrol, its use was discontinued entirely. Indeed no powder containing amyl alcohol was manufactured in France after October, 1910. Freshly manufactured *poudre BAm* smelled of amyl alcohol; the alcohol was converted by the products of the decomposition into the nitrous and nitric esters, and these soon broke down to produce red fumes anew and evil-smelling valerianic acid. The presence of the latter in the powder was easily detected, and was taken as evidence that the powder had become unstable. The Italians early used aniline as a stabilizer for their military ballistite. This forms nitro derivatives of aniline and of phenol, but it attacks nitrocellulose and is now no longer used. As early as 1909, diphenylamine was being used in the United States, in France, and in Germany, and, at the present time, it is the most widely used stabilizer in smokeless powder. The *centralites* (see below) also have a stabilizing action in smokeless powder but are used primarily as non-volatile solvents and deterrent coatings.

Calcium carbonate, either powdered limestone or precipitated chalk, is used as an anti-acid in dynamite where it serves as a satisfactory stabilizer. Urea is used in dynamite and in celluloid. It reacts with nitrous acid to produce nitrogen and carbon dioxide, and is unsuitable for use in smokeless powder because the gas bubbles destroy the homogeneity of the colloid and affect the rate of burning. The small gas bubbles however commend it for use in celluloid, for they produce an appearance of whiteness and counteract the yellowing of age.

In addition to the ability of certain substances to combine with the products of the decomposition of nitrocellulose, it is possible that the same or other substances may have a positive or a negative catalytic effect and may hasten or retard the decomposition by their presence. But it has not yet been made clear what types of chemical substance hasten the decomposition or why they do so. Nitrogen dioxide hastens it. Pyridine hastens it, and a powder containing 2 or 3% of pyridine will inflame spontaneously if heated for half an hour at 110°. Powders containing tetryl are very unstable, while those containing 10% of trinitronaphthalene (which does not react with the products of decomposition) are as

stable as those containing 2% of diphenylamine (which does react).

In a series of researches extending over a period of 15 years Marqueyrol<sup>11</sup> has determined the effect of various substances, particularly naphthalene, mononitronaphthalene, diphenylbenzamide, carbazol, diphenylamine, and diphenylnitrosamine, upon the stability of smokeless powder at 110°, 75°, 60°, and 40°. Samples of *poudre BF*<sup>12</sup> were made up containing different amounts of each stabilizer, and were subjected to dry heat in open vessels and in vessels closed with cork stoppers. Samples were removed from time to time and the nitrogen content of their nitrocellulose was determined. A sample of the powder was taken up in a solvent, and precipitated in a granular state; the precipitate was washed with cold chloroform until a fresh portion of chloroform was no longer colored by 18 hours contact with it, and was dried, and analyzed by the nitrometer. It was necessary to isolate the pure nitrocellulose and to separate it from the stabilizer, for the reason that otherwise the stabilizer would be nitrated in the nitrometer and a low result for nitrogen would be secured. A selected portion of Marqueyrol's results, from experiments carried out by heating in open vessels, are shown in the tables on

Days of heating at 40° . . . .	0	387	843	1174	2991	3945	4016
Analysis:							
no stabilizer . . . . .	201.8	199.5	147.8	199.5	199.2	198.9	198.2
2% amyl alcohol . . . . .	202.2	198.7	200.6	199.2	199.2	199.4	200.2
8% " " . . . . .	201.4	199.2	200.8	198.9	198.9	197.6	197.6
1% diphenylamine . . . . .	201.3	199.5	201.0	200.9	200.9	200.9	201.0
2% " " . . . . .	199.5	198.2	199.2	199.4	199.4	199.4	200.2
5% " " . . . . .	200.1	201.2	198.2	199.2	199.4	199.4	200.2
10% " " . . . . .	200.1	199.0	198.2	199.2	199.4	199.4	200.2
Days of heating at 60° . . . .	0	146	295	347	1059	2267	3935
Analysis:							
no stabilizer . . . . .	201.8	146.5	197.4	197.3	198.3	159.5	197.3
2% amyl alcohol . . . . .	202.2	197.4	197.3	198.3	159.5	197.3	197.3
8% " " . . . . .	201.4	197.3	197.3	198.3	159.5	197.3	197.3
1% diphenylamine . . . . .	201.3	197.6	197.6	200.0	197.6	197.6	197.6
2% " " . . . . .	199.5	196.1	196.1	198.3	196.1	196.1	196.1
5% " " . . . . .	200.1	196.0	196.0	196.0	196.0	196.0	185.7
10% " " . . . . .	200.1	192.3	192.3	192.3	192.3	192.3	173.0

<sup>11</sup> *Mém. poudres*, 23, 158 (1928).

<sup>12</sup> F = *fusil*, rifle.

Days of heating at 75°....	0	86	231	312	516	652	667
Analysis:							
2% amyl alcohol .....	203.1	<i>191.4</i>	.....	.....	.....	.....	.....
1% diphenylamine .....	201.3	196.0	.....	198.0	190.9	.....	.....
2% " .....	199.5	194.7	.....	198.1	.....	192.1	.....
5% " .....	200.1	.....	192.8	.....	.....	.....	186.2
10% " .....	200.1	.....	184.2	.....	.....	.....	175.9

Days of heating at 75°....	0	55	146	312	419	493	749
Analysis:							
1% diphenylnitrosamine	200.4	197.9	198.4	199.2	197.5	198.2	194.0
2% " .....	200.0	201.5	198.3	198.5	197.6	171.5	.....
10% " .....	201.5	195.3	194.1	193.0	190.6	187.3	184.3

Days of heating at 75°....	0	60	85	108	197	377	633
Analysis:							
2% amyl alcohol .....	200.9	198.9	<i>196.9</i>	.....	.....	.....	.....
1.25% carbazol .....	200.6	199.4	.....	199.1	<i>182.8</i>	.....	.....
10% " .....	200.3	198.7	.....	197.7	198.2	193.0	190.2

Days of heating at 75°....	0	31	50	62	87	227	556
Analysis:							
1.5% diphenylbenzamide	200.2	199.3	<i>186.1</i>	.....	.....	.....	.....
10% " .....	200.2	198.1	.....	.....	200.3	.....	.....
1.5% mononitronaphtha- lene .....	202.4	199.8	.....	.....	.....	.....	.....
10% mononitronaphtha- lene .....	202.0	198.1	.....	<i>193.0</i>	.....	.....	.....
1.5% naphthalene .....	202.3	200.2	194.8	.....	.....	.....	.....
10% " .....	201.8	199.2	.....	.....	.....	199.1	200.2

pages 309–310, where the numbers representing *analyses* indicate the nitrogen contents as usually reported in France, namely, cubic centimeters of nitric oxide per gram of nitrocellulose. When the numbers are printed in italics, the samples which were taken for analysis were actively giving off red nitrous fumes.

Diphenylnitrosamine, which is always present in powders made from diphenylamine, is decomposed at 110°, and that temperature therefore is not a suitable one for a study of the stability of smokeless powder. At 75° diphenylnitrosamine attacks nitrocellulose less rapidly than diphenylamine itself, but this is not true at lower temperatures (40° and 60°) at which there is no appreciable difference between the two substances. Carbazol at 110° is an excellent stabilizer but at 60° and 75° is so poor as to

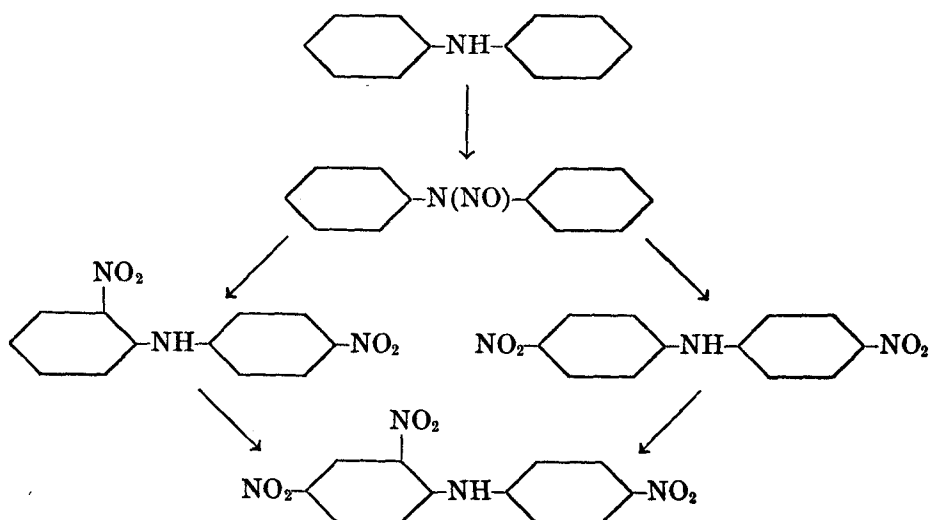


deserve no further consideration. Ten per cent of diphenylamine gives unstable smokeless powder. Powder containing 40% of diphenylamine inflames spontaneously when heated in an open vessel at 110° for an hour and a half. Diphenylamine attacks nitrocellulose, but it does not attack it as rapidly as do the products themselves of the decomposition of nitrocellulose in air; and 1 or 2% of the substance, or even less, in smokeless powder is as good a stabilizer as has yet been found.

### Transformations of Diphenylamine During Aging of Powder

Desmaroux,<sup>13</sup> Marquoyrol and Muraour,<sup>14</sup> and Marquoyrol and Loriette<sup>15</sup> have studied the diphenylamine derivatives which give a dark color to old powder, and have concluded that they are produced by impurities in the ether which is used in the manufacture or by the oxidizing action of the air during drying and storage. Their presence is not evidence that the powder has decomposed, but indicates that a certain amount of the diphenylamine has been consumed and that correspondingly less of it remains available for use as a stabilizer.

The transformations of diphenylamine<sup>16</sup> in consequence of its reaction with the products of the decomposition of nitrocellulose are indicated by the following formulas. None of these substances imparts any very deep color to the powder.



<sup>13</sup> *Mém. poudres*, 21, 238 (1924).

<sup>14</sup> *Ibid.*, 21, 259, 272 (1924).

<sup>15</sup> *Ibid.*, 21, 277 (1924).

<sup>16</sup> Davis and Ashdown, *Ind. Eng. Chem.*, 17, 674 (1925).

The diphenylamine is converted first into diphenylnitrosamine which is as good a stabilizer as diphenylamine itself. Since both of these substances may be detected by simple tests upon an alcoholic extract of a sample of the powder, the fitness of the powder for continued storage and use may be easily demonstrated. A strip of filter paper on which the alcoholic extract has been allowed to evaporate is colored blue by a drop of ammonium persulfate solution if unchanged diphenylamine is present. Likewise the extract, if it contains diphenylamine, is colored blue by the addition of a few drops of a saturated aqueous solution of ammonium persulfate. Since the alcoholic extract is often colored, the test is best carried out by comparing the colors of two equal portions of the extract, one with and one without the addition of ammonium persulfate. Diphenylnitrosamine gives no color with ammonium persulfate. One-tenth of a milligram of diphenylnitrosamine imparts an intense blue color to a few cubic centimeters of cold concentrated sulfuric acid. It gives no color with a cold 1% alcoholic solution of  $\alpha$ -naphthylamine, but an orange color if the solution is heated.<sup>17</sup> None of the other diphenylamine derivatives which occur in smokeless powder give these tests.

Diphenylnitrosamine rearranges under the influence of mineral acids to form *p*-nitrosodiphenylamine. The latter substance is evidently formed in smokeless powder and is oxidized and nitrated by the products of the decomposition to form 2,4'- and 4,4'-dinitrodiphenylamine. Davis and Ashdown<sup>16</sup> have isolated both of these substances from old powder, and have also prepared<sup>17</sup> them by the nitration of diphenylnitrosamine in glacial acetic acid solution. Both substances on further nitration yield 2,4,4'-trinitrodiphenylamine, which represents the last stage in the nitration of diphenylamine by the products of the decomposition of smokeless powder. This material has been isolated from a sample of U. S. pyrocellulose powder which was kept at 65° in a glass-stoppered bottle for 240 days after the first appearance of red fumes. The several nitro derivatives of diphenylamine may be distinguished by color reactions with alcoholic solutions of ammonia, sodium hydroxide, and sodium cyanide, and some insight into the past history of the powder may be gained from tests on the alcohol extract with these reagents, but their pres-

<sup>17</sup> Davis and Ashdown, *J. Am. Chem. Soc.*, **46**, 1051 (1924).

ence is evidence of instability, and no powder in which the diphenylnitrosamine is exhausted is suitable for further storage and use.

**Absorption of Moisture**<sup>18</sup>

Nitrocellulose itself is hygroscopic, but its tendency to take up moisture is modified greatly by other substances with which it is incorporated. Colloided with nitroglycerin in the absence of solvent, it yields a product which shows no tendency to take up moisture from a damp atmosphere. Colloided with ether-alcohol, as in the case of the *poudre B* and the straight pyrocellulose powders which were used in the first World War, it yields a powder which is hygroscopic both because of the hygroscopicity of the nitrocellulose itself and because of the hygroscopicity of the alcohol and ether which it contains. In water-dried powder the alcohol and ether of the surface layer have been largely removed or replaced with water, the hygroscopicity of the surface layer is reduced, and the interior of the grain is prevented to a considerable extent from attracting to itself the moisture which it would otherwise attract. In certain coated and *progressive burning* powders, the surface layers are made up of material of greatly reduced hygroscopicity and the interiors are rendered inaccessible to atmospheric influences.

The tendency of straight nitrocellulose powder to take up moisture and the effect of the absorbed moisture in reducing the ballistic power of the powder are shown by the table below.

Period of exposure, hrs. ....	0	24	48	72	96
Total volatiles, % .....	3.26	3.55	3.71	3.84	3.93
External moisture, % .....	1.02	1.15	1.40	1.47	1.57
Residual solvent, % .....	2.24	2.40	2.31	2.37	2.35
Velocity, ft. per sec. ....	1706.6	1699.0	1685.4	1680.4	1669.0
Pressure, lb. per sq. in. ....	31,100	31,236	30,671	29,636	28,935

A sample of water-dried powder was exposed to an atmosphere practically saturated with water vapor. Portions were removed each day; one part was fired in the gun, and another part was analyzed for *total volatile matter* (TV) and for volatile matter driven off by an hour's heating at 100° (*external moisture*, EM).

<sup>18</sup> Cf. Davis, *Army Ordnance*, 2, 9 (1921).

The amount of total volatile matter increased regularly during the period of exposure, as did also the amount of volatile matter resident at or near the surface of the powder grains. The amount of volatile matter in the interior of the powder grains (*residual solvent*, RS) did not alter materially during the experiment.

Total volatiles in powder is determined by dissolving the sample in a solvent, precipitating in a porous and granular condition, evaporating off the volatile matter, and drying the residue to constant weight. External moisture is the amount of volatile matter which is driven off by some convenient method of desiccation. The difference between the two is residual solvent,  $TV - EM = RS$ , and is supposed to correspond to volatile matter resident within the interior of the grain and not accessible to desiccating influences. Various methods of determining external moisture have been in use among the nations which use straight nitrocellulose powder and in the same nation among the manufacturers who produce it. At the time of the first World War, for example, external moisture was determined in Russia by heating the sample at  $100^{\circ}$  for 6 hours, in France by heating at  $60^{\circ}$  for 4 hours, and in the United States by heating at  $60^{\circ}$  in a vacuum for 6 hours. These several methods, naturally, all give different results for external moisture and consequently different results for residual solvent.

There appears really to be no method by which true external moisture may be determined, that is, no method by which only the surface moisture is removed in such fashion that the residual solvent in the powder is found to be the same both before and after the powder has been allowed to take up moisture. Samples of powder were taken and residual solvent was determined by the several methods indicated in the next table. The samples were exposed 2 weeks to an atmosphere practically saturated with water vapor, and residual solvent was again determined as before. The surprising result was secured in every case, as indicated, that the amount of residual solvent was less after the powder had been exposed to the moist atmosphere than it was before it had been exposed. Yet the powder had taken up large quantities of moisture during the exposure. It is clear that the exposure to the moist atmosphere had made the volatile matter of the interior of the grains more accessible to desiccating influ-

ences. Evidently the moisture had opened up the interior of the grains, presumably by precipitating the nitrocellulose and producing minute cracks and pores in the colloid. Verification of this explanation is found in the effect of alcohol on colloided pyrocellulose powder. The powder took up alcohol from an atmosphere saturated with alcohol vapor, but alcohol does not precipitate the colloid, it produces no cracks or pores, and in every case residual solvent was found to be greater after the powder had been exposed to alcohol vapor than it had been before such exposure. The following table shows data for typical samples of powder before and after exposures of 2 weeks to atmospheres saturated respectively with water and with alcohol.

Method of Determining External Moisture and Residual Solvent	Exposure to Water Residual solvent			Exposure to Alcohol Residual solvent		
	Be-fore	After	Differ-ence	Be-fore	After	Differ-ence
1 hr. at 100° in open oven..	3.12	2.82	-0.30	2.41	4.57	+2.16
6 hrs. at 100° in open oven..	2.81	2.36	-0.45	2.22	3.92	+1.70
6 hrs. at 55° in vacuum.....	2.91	2.54	-0.37	2.27	4.10	+1.83
55° to constant weight in open oven.....	3.00	2.72	-0.28	2.58	4.25	+1.67
Over sulfuric acid to constant weight.....	2.95	2.39	-0.56	2.32	4.10	+1.78

Samples of pyrocellulose powder, varying in size from 0.30 caliber single-perforated to large multiperforated grains for the 10-inch gun, were exposed to a moist atmosphere until they no longer gained any weight. They were then desiccated by the rather vigorous method of heating for 6 hours at 100°. All the samples lost more weight than they had gained. As the exposures to moisture and subsequent desiccations were repeated, the differences between the weights gained by taking up moisture and the weights lost by drying became less and less until finally the powders on desiccation lost, within the precision of the experiments, exactly the amounts of volatile matter which they had taken up. At this point it was judged that all residual solvent had

been driven out of the powder and that further treatment would produce no additional cracks and pores in the grains. The gain or loss (either one, for the two were equal) calculated as per cent of the weight of the desiccated sample gave the apparent hygroscopicities listed below. Since all the powders were made from the

CALIBER	APPARENT HYGROSCOPICITY, %
0.30	3.00
75 mm.	2.75
4.7 inches	2.42
6 inches	2.41
10 inches	2.11

same material, namely, straight pyrocellulose, the differences in the apparent hygroscopicity are presumed to be caused by the drying treatment not being vigorous enough to drive out all the moisture from the interior of the grains of greater web thickness. The drying, however, was so vigorous that the powders became unstable after a few more repetitions of it. The losses on desiccation became greater because of decomposition, and the gains on exposure to moisture became greater because of the hygroscopicity of the decomposition products.

Although hygroscopicity determined in this way is apparent and not absolute, it supplies nevertheless an important means of estimating the effects both of process of manufacture and of composition upon the attitude of the powder toward moisture. Thus, samples of pyrocellulose powder for the 4.7-inch gun, all of them being from the same batch and pressed through the same die, one air-dried, one water-dried, one dried under benzene at 60°, and one under ligroin at 60°, showed apparent hygroscopicities of 2.69%, 2.64%, 2.54%, and 2.61%, which are the same within the experimental error. Milky grains<sup>19</sup> of 75-mm. powder showed an apparent hygroscopicity of 2.79%, compared with 2.75% for the normal amber-colored grains. The experiment with this powder was continued until considerable decomposition was evident; the successive gains and losses were as follows, calculated as per cent of the original weight of the sample.

<sup>19</sup> Grains which had a milky appearance because of the precipitation of the colloid during the water-dry treatment. This result follows if the grains contain more than 7 or 7.5% of ether-alcohol when they are submitted to water-drying.

GAIN, %	Loss, %
2.315	3.030
2.439	2.623
2.259	2.337
2.279	2.319
2.179	2.577
2.448	2.554
2.325	2.630
2.385	3.022

Experiments with 75-mm. powders, made from pyrocellulose with the use of ether-alcohol and with various other substances incorporated in the colloids, gave the following results for hygroscopicity. Hydrocellulose does not dissolve in the nitrocellulose

Pyrocellulose with		
5%	hydrocellulose	2.79%
10%	crystalline DNX	2.09%
10%	DNX oil	1.99%
10%	crystalline DNT	1.93%
15%	" "	1.41%
20%	" "	1.23%
25%	" "	1.06%

colloid, and does not affect its hygroscopicity. The aromatic nitro compounds dissolve, and they have a marked effect in reducing the absorption of moisture. They are explosive non-volatile solvents and contribute to the energy of the powder.

Other non-volatile solvents which are not explosive are discussed below in the section on gelatinizing agents. These tend to reduce the potential of the powder, but their action in this respect is counteracted in practice by using guncotton in place of part or all the nitrocellulose. The guncotton is colloided by the gelatinizing agent, either in the presence or in the absence of a volatile solvent, and the resulting powder is non-hygroscopic and as strong or stronger than straight pyrocellulose powder.

### Control of Rate of Burning

Cordite is *degressive* burning, for its burning surface decreases as the burning advances. Powder in strips, in flakes, and in single-perforated tubes has a burning surface which is very nearly constant if the size of the strips or flakes, or the length of the tubes, is large relative to their thickness. Multiperforated grains are *progressive* burning, for their burning surface actually increases

as the burning advances, and, other things in the gun being equal, they produce gas at a rate which accelerates more rapidly and, in consequence, gives a greater velocity to the projectile.

A progressive burning strip ballistite was used to some extent by the French in major caliber guns during the first World War. It consisted of a central thick strip or slab of ballistite, 50%

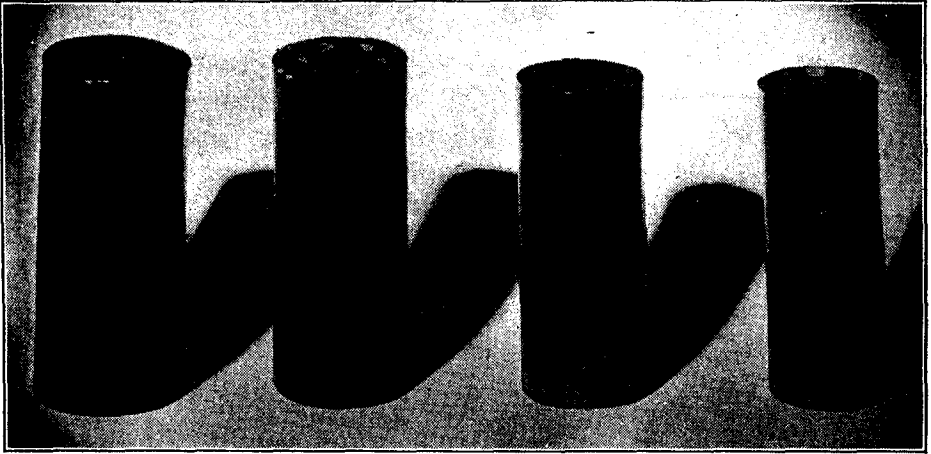


FIGURE 79. Progressive Burning Colloided Smokeless Powder. 12-Inch powder at different stages of its burning. A grain of 12-inch powder, such as appears at the left, was loaded into a 75-mm. gun along with the usual charge of 75-mm. powder (of the same form as the 12-inch grain but of less web thickness). When the gun was fired, a layer of colloid having a thickness equal to one-half the web of the 75-mm. powder was burned off from every grain in the gun. This consumed the 75-mm. powder completely. The 12-inch grain was extinguished when thrown from the muzzle of the gun; it was picked up from the ground—and is the second grain in the above picture. The next grain was shot twice from a 75-mm. gun, the last grain three times. After three shootings, the perforations are so large that a fourth shooting would cause them to meet one another, and the grain to fall apart, leaving slivers.

nitroglycerin and 50% soluble nitrocellulose, made without volatile solvent, and sandwiched between two thin strips of powder made, without volatile solvent, from 50% soluble nitrocellulose and 50% crystalline dinitrotoluene. The two compositions were rolled to the desired thicknesses separately between warm rolls, and were then combined into the laminated product by pressing between warm rolls. The outer layers burned relatively slowly with a temperature of about 1500°; the inner slab burned rapidly with a temperature of about 3000°.



Progressive burning *coated powders*, usually flakes or single-perforated short cylinders, are made by treating the grains with a gelatinizing agent, or non-volatile, non-explosive solvent for nitrocellulose, dissolved in a volatile liquid, generally benzene or acetone, tumbling them together in a sweetie barrel or similar device, and evaporating off the volatile liquid by warming while the tumbling is continued. The material which is applied as a coating is known in this country as a *deterrent*, in England as a

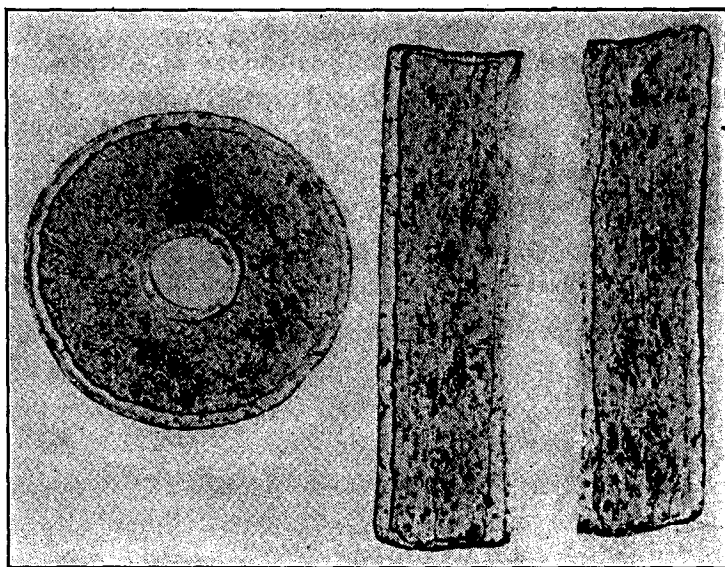


FIGURE 80. Cross Section and Longitudinal Section of a Grain of .50 Caliber Extruded Smokeless Powder, Deterrent Coated (25 $\times$ ). (Courtesy Western Cartridge Company.)

*moderant*. At the time of the first World War *sym*-dimethyldiphenylurea was already used widely as a deterrent in rifle powder intended for use in shooting matches and in military propellants designed to produce especially high velocities. The substance was called *centralite* because its use had been developed in Germany at the Central War Laboratory at Spandau. The ethyl analog, diethyldiphenylurea, at first known as *ethyl centralite*, is usually called Centralite No. 1 and has generally superseded the methyl compound (or Centralite No. 2) for use in smokeless powder. Although many other substances have been tried and have been patented, this remains the most widely used of any. *Butyl centralite* is a better gelatinizing agent for nitrocellulose than either

the methyl or the ethyl compound, and is likely to find more extensive use in the future.

### Gelatinizing Agents

Gelatinizing agents, of which the centralites are examples, are often incorporated in colloided straight nitrocellulose and double-base powders where they cause the materials to burn more slowly, where they serve as flash reducing agents, and where they reduce the tendency of the powders to take up moisture. They reduce the amount of volatile solvent which is needed in the manufacture of nitrocellulose powders, and facilitate the manufacture of double-base powders without any volatile solvent at all. The centralites happen also to be effective stabilizers, but this is not a general property of gelatinizing agents.

Marqueyrol and Florentin<sup>20</sup> have published a list of patents for gelatinizing agents, esters, amides, urea derivatives, halogen compounds, ketones, and alcohols, and have reported their study of many of them with respect to their effectiveness on the CP<sub>1</sub> and CP<sub>2</sub>, insoluble and soluble nitrocellulose respectively, which were standard in the French service. To a weighed quantity of the dry nitrocellulose a dilute solution of the gelatinizing agent in 95% alcohol was added in portions of 1 cc. at a time, the alcohol was then evaporated at a temperature of 35–40°, more of the alcohol solution was added, and the evaporation was repeated until gelatinization was complete. The results with the best gelatinizing agents are shown in the table below, where the numbers

	CP <sub>1</sub> (INSOLUBLE)	CP <sub>2</sub> (SOLUBLE)
Ethyl sebacate .....	320	65
Dimethylphenyl-o-tolylurea .....	260	65
Dimethyldiphenylurea .....	...	80
Ethyl succinate .....	400	90
Ethyl phthalate .....	360	95

represent the amounts by weight of the several substances which were needed for the complete gelatinization of 100 parts of the nitrocellulose. Ninety parts of ethyl citrate or of benzyl benzoate almost completely gelatinized 100 parts of CP<sub>2</sub>, 90 of ethyl malonate incompletely, 90 of ethyl oxalate or of ethyl stearate more incompletely, and 90 of ethyl acetoacetate or of ethyl ricinoleate

<sup>20</sup> *Mém. poudres*, 18, 150, 163 (1921).

but very little. Four hundred parts of triphenyl phosphate almost completely gelatinized 100 parts of CP<sub>1</sub>, and 400 of ethyl malonate or of ethyl oxalate produced only incomplete gelatinization.

Marqueyrol and Florentin point out that the lower members of the series of esters, the acetates, butyrates, valerates, etc., are good solvents for nitrocellulose—ethyl and amyl acetate have long been used for the purpose—but the higher members, the stearates and oleates, gelatinize nitrocellulose but very little. To the esters of the dibasic acids the opposite rule appears to apply; the higher members are better than the lower. Acetone is a well-known solvent both for soluble and for “insoluble” nitrocellulose, but acetophenone gelatinizes even soluble nitrocellulose only feebly.

Experiments by the present writer<sup>21</sup> with a variety of other gelatinizing agents have shown that the amounts necessary to produce complete gelatinization of pyrocellulose are different if different solvents are used for applying them. In general they are more effective in benzene than in alcohol, and more in alcohol than in ligroin. Half-gram samples of dry pyrocellulose were treated in 30-cc. beakers with known quantities of the gelatinizing agents dissolved in convenient volumes (15–30 cc.) of alcohol, benzene, or ligroin. The volatile liquids were evaporated off slowly at 60°, the residues were warmed at 60° for 10 minutes longer (during which time a considerable improvement in the gelatinization was generally observed), and were then examined to determine their condition. If complete gelatinization had not occurred, other experiments were carried out with fresh samples. The results, summarized in the table on page 322, are accurate to the nearest 10%. They support several conclusions. *Sym*-dialkyl ureas are excellent gelatinizing agents for nitrocellulose, and the property remains if additional aliphatic or aromatic groups are introduced into the molecule. The heavier the alkyl groups, the greater appears to be the gelatinizing power. Of the aromatic substituted ureas, those in which there are less than three aromatic groups appear to be without action. Among the alkyl esters of sebacic and phthalic acids, those which contain the heavier alkyl groups are generally the better gelatinizing agents. The alkyl esters of aliphatic and of aromatic substituted

<sup>21</sup> Davis, *Ind. Eng. Chem.*, **14**, 1140 (1922).

PARTS BY WEIGHT NECESSARY FOR THE COMPLETE GELATINIZATION OF  
100 PARTS OF PYROCELLULOSE

	In Alcohol	In Benzene	In Ligroin
Methylurea .....	No action	with 100 parts	
Ethyleneurea .....	No action	with 100 parts	
<i>Sym</i> -dimethylurea .....	60	70	...
<i>Sym</i> -diethylurea .....	50	50	...
<i>Unsym</i> -dimethylurea .....	No action	with 100 parts	
Tetramethylurea .....	80	...	...
Benzylurea .....	No action	with 100 parts	
<i>Sym</i> -diphenylurea .....	No action	with 100 parts	
<i>Sym</i> -di- <i>p</i> -tolylurea .....	No action	with 100 parts	
<i>Unsym</i> -diphenylurea .....	No action	with 100 parts	
Triphenylurea .....	...	35	...
$\alpha,\alpha$ -diphenyl- <i>p</i> -tolylurea .....	...	40	...
Tetraphenylurea .....	No action	30	...
	with 160 parts		
Ethyltriphenylurea .....	80	...	...
<i>Sym</i> -dimethyldiphenylurea .....	70	25	...
<i>Sym</i> -diethyldiphenylurea .....	70	30	...
<i>Sym</i> -di- <i>n</i> -butyldiphenylurea .....	60	20	...
<i>Unsym</i> -dimethyldiphenylurea .....	60	...	...
Carbamic acid ethyl ester .....	140	80	...
Methylcarbamic acid ethyl ester .....	90	60	...
Ethylcarbamic acid ethyl ester .....	90	60	...
Phenylcarbamic acid ethyl ester .....	20	90	...
Phenylcarbamic acid phenyl ester .....	No action	with 200 parts	
Phenylcarbamic acid benzyl ester .....	No action	with 100 parts	
Diphenylcarbamic acid phenyl ester .....	80	70	...
Methyl sebacate .....	80	70	105
Ethyl sebacate .....	80	50	90
Iso-amyl sebacate .....	70	95	90
Methyl phthalate .....	95	70	115
Ethyl phthalate .....	95	50	100
Iso-amyl phthalate .....	95	50	80
DNX oil .....	120	130	330
Trinitrotoluene .....	...	300	...

carbamic acids are excellent gelatinizing agents, but the aromatic esters appear to be without action unless the total number of aromatic groups is equal to three.

### Flashless Charges and Flashless Powder

The discharge of a machine gun shooting ordinary charges of smokeless powder produces bright flashes from the muzzle which

at night disclose the position of the gun to the enemy. When a large gun is fired, there is a large and dazzlingly bright muzzle flash, from a 12-inch gun for example a white-hot flame 150 feet or more in length. The light from such a flame reflects from the heavens at night and is visible for a distance of as much as 30 miles, much farther than the sound from the gun may be heard. The enemy by the use of appropriate light-ranging apparatus may determine the position of the flash, and may undertake to bombard and destroy the battery from a great distance.

Smokeless powder, burning in the chamber of the gun at the expense of its own combined oxygen, produces gas which contains hydrogen, carbon monoxide, carbon dioxide, etc., and this gas, being both hot and combustible, takes fire when it emerges from the muzzle and comes into contact with the fresh oxygen supply of the outer air. One part of the brilliancy of the flash is the result of the emergent gas being already preheated, often to a temperature at which it would be visible anyway, generally to a point far above the temperature of its inflammation in air. In thinking about this latter temperature, it is necessary to take account of the fact that, other things being equal, a small cloud of gas from a small gun loses its temperature more quickly and becomes completely mixed with the air more rapidly than a large cloud of gas from a large gun. The gas emerging from a small gun would need to be hotter in the first place if it is to inflame than gas of the same composition emerging from a large gun. It is for this reason perhaps that it is easier to secure flashless discharges with guns of small caliber (not over 6 inch) than with those of major caliber.

There are four ways, distinguishably different in principle, by which flashlessness has been secured, namely,

(1) by the addition to the charge of certain salts, particularly potassium chloride or potassium hydrogen tartarate, or by the use of powdered tin or of some other substance which, dispersed throughout the gas from the powder, acts as an anti-oxidant and prevents its inflammation;<sup>22</sup>

(2) by incorporating carbonaceous material in the smokeless powder, by which means the composition of the gas is altered and

<sup>22</sup> Cf. Demougin, *Mém. poudres*, 25, 130 (1932-33); Fauveau and Le Paire, *ibid.*, 25, 142 (1932-33); Prettre, *ibid.*, 25, 160, 169 (1932-33).

the number of mols of gas is actually increased while the temperature is lowered;

(3) by incorporating in the powder a *cool explosive*, such as ammonium nitrate, guanidine nitrate, or nitroguanidine, which explodes or burns with the production of gas notably cooler than the gas from the combustion of ordinary smokeless powder; and

(4) by contriving the ignition of the powder, the acceleration of its burning rate, and the design of the gun itself, any or all these factors, in such fashion that the projectile takes up energy from the powder gas more quickly and more effectively than is ordinarily the case, and thereby lowers the temperature of the gas to a point where the flash is extinguished.

The first of these methods is applicable to all calibers; the second and the third are successful only with calibers of less than 6 inches; the fourth has not yet been sufficiently studied and exploited. It is true, however, that an improved igniter, with the same gun and with the same powder, may determine the difference between a flash and a flashless discharge.

The use of salts to produce flashlessness appears to derive from an early observation of Dautriche that a small amount of black powder, added to the smokeless powder charge of small-arms ammunition, makes the discharge flashless. During the first World War the French regularly loaded a part of their machine gun ammunition with a propellant consisting of 9 parts of smokeless powder and 1 of black powder.

The Germans in their cannon used *anti-flash bags* or *Vorlage*, loaded at the base of the projectiles, between the projectiles and the propelling charges. These consisted of two perforated discs of artificial silk or cotton cloth sewed together in the form of doughnut-shaped bags. The bags were filled with coarsely pulverized potassium chloride. The artillerymen were not informed of the nature of the contents of the bags but were advised against using any whose contents had hardened to a solid cake, and were instructed in their tactical use as follows.

In firing with *Vorlage*, there is produced a red fire [a red glow] at the muzzle and in front of the piece. The smoke is colored red [by the glow]. This light however gives no reflection in the heavens. In fact it is visible and appreciable at a distance only if the piece is placed in such a way that

the enemy can see its muzzle. In the daytime, *Vorlage* must be used only when the weather is so dark that the flashes of the shots without them are more visible than the clouds of smoke which they produce. The opaqueness of the background against which the battery stands out or the obscurity of the setting which surrounds it are also at times of a kind to justify the use of *Vorlage* in the daytime.

The anti-flash bags reduced the range by 4.5 to 8%.

Fauveau and Le Paire <sup>23</sup> studied the anti-flash effect of potassium chloride and of other salts and concluded that the lowering of the temperature of the gas which undoubtedly results from their volatilization and dissociation is insufficient to account for the extinction of the flash. Prettre <sup>24</sup> found that the chlorides of sodium and of lithium, and other alkali metal salts which are volatile, had the same effect as potassium chloride. He found that small amounts of potassium chloride, volatilized in mixtures of carbon monoxide and air, had a powerful anti-oxidant action and a correspondingly large effect in raising the temperature of inflammation of the gas. Some of his results are shown in the table below. He found that potassium chloride was without effect

MILLIGRAMS OF KCl PER LITER OF GASEOUS MIXTURE	TEMPERATURE (°C.) OF INFLAMMATION OF AIR CONTAINING		
	24.8% CO	44.1% CO	67.3% CO
0.0.....	656	657	680
0.4.....	...	750	800
0.5.....	730	...	820
0.7.....	...	810	900
1.0.....	790	850	1020
1.3.....	810	...	...
2.0.....	890	950	...
2.5.....	...	1000	...
3.0.....	970	...	...
3.5.....	1010	...	...

upon the temperature of inflammation of mixtures of hydrogen and air.

The French have used anti-flash bags (*sachets antilueurs*) filled with the crude potassium hydrogen tartarate (about 70%

<sup>23</sup> *Loc. cit.*

<sup>24</sup> *Loc. cit.*

pure) or *argols* which is a by-product of the wine industry. The flat, circular, cotton bags containing the argols were assembled along with the smokeless powder and black powder igniter in silk cartridge bags to make up the complete charge. Since the anti-flash material tended to reduce the ballistic effect of the charge, it was necessary when firing flashless rounds to add an *appoint* or additional quantity of smokeless powder. Thus, for ordinary firing of the 155-mm. gun, the charge consisted of 10 kilograms of *poudre BM7* along with an igniter system containing a total of 115 grams of black powder. For a flashless round, 3 *sachets* containing 500 grams of argols each were used and an additional 305 grams of smokeless powder to restore the ballistics to normal.

Another method of securing flashlessness was by the use of pellets (*pastilles*) of a compressed intimate mixture of 4 parts of potassium nitrate and 1 part of crystalline DNT. Pellets for use in the 155-mm. gun weighed 1 gram each, and were about 2 mm. thick and 15 mm. in diameter. Two or three hundred of these were sewed up in a silk bag which was loaded into the gun along with the bag containing the powder. The pellets burned with the same velocity as *poudre B*, and had but very little effect upon the ballistics. They of course produced a certain amount of smoke and the discharge gave a red glow from the muzzle of the gun.

Oxanilide functions well as an anti-flash agent if it is distributed throughout the powder charge, but not if it is loaded into the gun in separate bags like the materials which have just been mentioned. It is made into a thick paste with glue solution, the paste is extruded in the form of little worms or pellets, and these are dried. Pellets to the amount of 15% of the powder charge produce flashlessness in the 6-inch gun, but the charge is more difficult to light than ordinarily and requires a special igniter.

Oxanilide and many other carbonaceous materials, incorporated in the grains of colloided powder, yield powders which are flashless in guns of the smaller calibers and, in many cases, are as powerful, weight for weight, as powders which contain none of the inert, or at least non-explosive, ingredients. If nitrocellulose burning in the gun produces 1 mol of carbon dioxide and a certain amount of other gaseous products, then nitrocellulose plus 1 mol of carbon under the same conditions will produce 2 mols of



carbon monoxide along with substantially the same amount of the other gaseous products. There will be more gas and cooler gas. A colloid powder made from pyrocellulose 85 parts and hydrocellulose 15 parts is flashless in the 75-mm. gun, and gives practically the same ballistic results as a hotter and more expensive powder made from straight nitrocellulose. The strength of the powder may be increased without affecting its flashlessness by substituting part of the pyrocellulose by guncotton of a higher nitrogen content.

Among the materials which have been incorporated into colloid powder for the purpose of reducing or extinguishing the flash are (1) substances, such as starch, hydrocellulose, and anthracene, which are insoluble in the colloid and are non-explosive. They, of course, must exist in a state of fine subdivision to be suitable for this use. Other anti-flash agents are (2) solid or liquid non-explosive substances, such as diethyldiphenylurea and dibutyl phthalate, which are solvents for nitrocellulose and dissolve in the colloid. They reduce the hygroscopicity of the powder and they reduce the amount of volatile solvent which is needed for the manufacture. Still others are (3) the explosive solid and liquid aromatic nitro compounds which are solvents for nitrocellulose and are effective in reducing both the flash and the hygroscopicity. All or any of the substances in these three classes may be used either in a straight nitrocellulose or in a nitrocellulose-nitroglycerin powder. Several flashless powders have been described in the section on the "Classification of Smokeless Powders." Many varieties have been covered by numerous patents. We cite only a single example,<sup>25</sup> for a smokeless, flashless, non-hygroscopic propellant powder made from about 76–79% nitrocellulose (of at least 13% nitrogen content), about 21–24% dinitrotoluene, and about 0.8–1.2% diphenylamine. During the first World War the French and the Italians used a *superattenuated* ballistite, made without volatile solvent, and containing enough aromatic dinitro compound (in place of part of the nitroglycerin) to make it flashless. In a typical case the powder was made from 30 parts CP<sub>1</sub>, 30 CP<sub>2</sub>, 15 DNT, and 25 nitroglycerin.

<sup>25</sup> U. S. Pat. 2,228,309 (1941), Ellsworth S. Goodyear.

### Ball-Grain Powder

The process for the manufacture of ball-grain powder which Olsen and his co-workers have devised<sup>26</sup> combines nicely with Olsen's process for the quick stabilization of nitrocellulose to form a sequence of operations by which a finished powder may be produced more rapidly and more safely than by the usual process. It supplies a convenient means of making up a powder which contains non-volatile solvents throughout the mass of the grains or deterrent or accelerant coatings upon their surface.

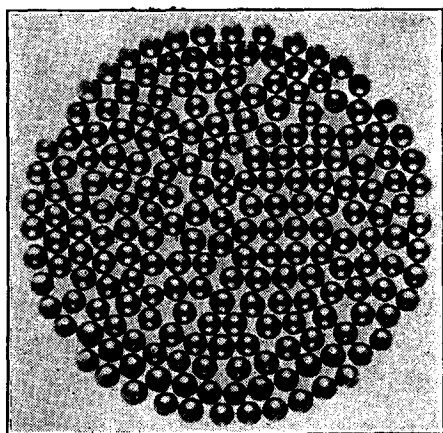


FIGURE 81. Ball Grains (Smokeless Powder) (3X). (Courtesy Western Cartridge Company.)

Nitrocellulose, pulped and given a preliminary or sour boiling, may be used directly without poaching. Deteriorated smokeless powder, containing nitro derivatives of diphenylamine and acidic decomposition products, may be reduced to a coarse powder under water in a hammer mill, and may then be used. Whichever is used, the first necessity is to stabilize it by complete removal of the acid. For this purpose, the material in the presence of water (which may contain a little chalk in suspension or urea in solution) is introduced into a still where it is dissolved with agitation in ethyl acetate to form a heavy syrup or lacquer, and is treated with some substance which is adsorbed by nitrocellulose more readily than acid is adsorbed. It is a curious fact that nitrocellulose is dissolved or dispersed by ethyl acetate much more readily

<sup>26</sup> U. S. Pat. 2,027,114 (1936), Olsen, Tibbitts, and Kerone; also U. S. Pats. 2,111,075 (1938), 2,175,212 (1939), 2,205,916 (1940).

in the presence of water than when water is absent. Diphenylamine is dissolved in the ethyl acetate before the latter is added to the water and nitrocellulose in the still. At the same time, centralite or DNT or any other substance which it may be desired to incorporate in the powder is also dissolved and added. The water phase and the lacquer are then stirred for 30 minutes by which operation the nitrocellulose is stabilized.<sup>27</sup> Starch or gum arabic solution to secure the requisite colloidal behavior is then introduced into the still, the still is closed, the temperature is raised so that the lacquer becomes less viscous, and the mixture

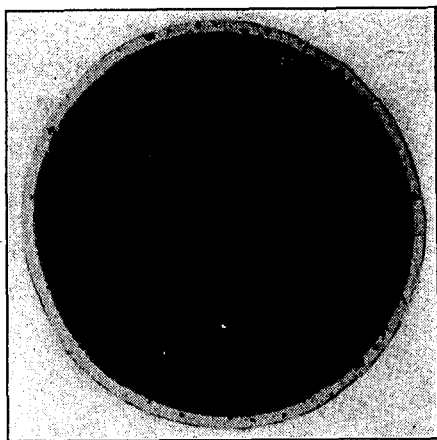


FIGURE 82. Cross Section of Ball Grain, Double Base, Deterrent Coated (112 $\times$ ). (Courtesy Western Cartridge Company.)

under pressure is agitated vigorously until the lacquer is broken up into small globules of the correct size. The pressure is then reduced, and the ethyl acetate is distilled off and recovered. If the distillation is carried out too rapidly, the grains are shaped like kernels of popcorn. If it is carried out at such a rate that the volatile solvent is evaporated from the surface of the globules no faster than it moves from the interior to the surface, if the distillation is slow at first and more rapid afterwards, then smooth ball grains are formed, dense and of homogeneous structure.

<sup>27</sup> Diphenylamine in the presence of water thus has an action beyond that which it has when it is added to the nitrocellulose gel (in the absence of a separate water phase) during the manufacture of smokeless powder by the usual process. Being preferentially adsorbed by the nitrocellulose, it drives any acid which may be present out of the nitrocellulose and into the water. After that it fulfils its usual function in the powder.

After the material has cooled, the powder grains are transferred in a slurry to another still and are treated with an emulsion of nitroglycerin dissolved in toluene, or of some other coating agent dissolved in a solvent in which nitrocellulose itself is insoluble, and the volatile solvent is distilled off, leaving the nitroglycerin or other material deposited on the surface of the grains. As much nitroglycerin as 15% of the weight of the powder may be applied in this way. A coating of centralite may, if desired, be put on top of it. The grains are sieved under water and are then dried for use in shotguns. If the powder is to be used in rifles, it is passed in a slurry between warm steel rollers by which all the grains are reduced to the same least dimension or web thickness. Previous to the drying, all the operations in the manufacture of ball-grain powder are carried out under water, and are safe. After the drying, the operations involve the same hazards, by no means insurmountable, as are involved in the ordinary process. The grains are glazed with graphite and blended.