

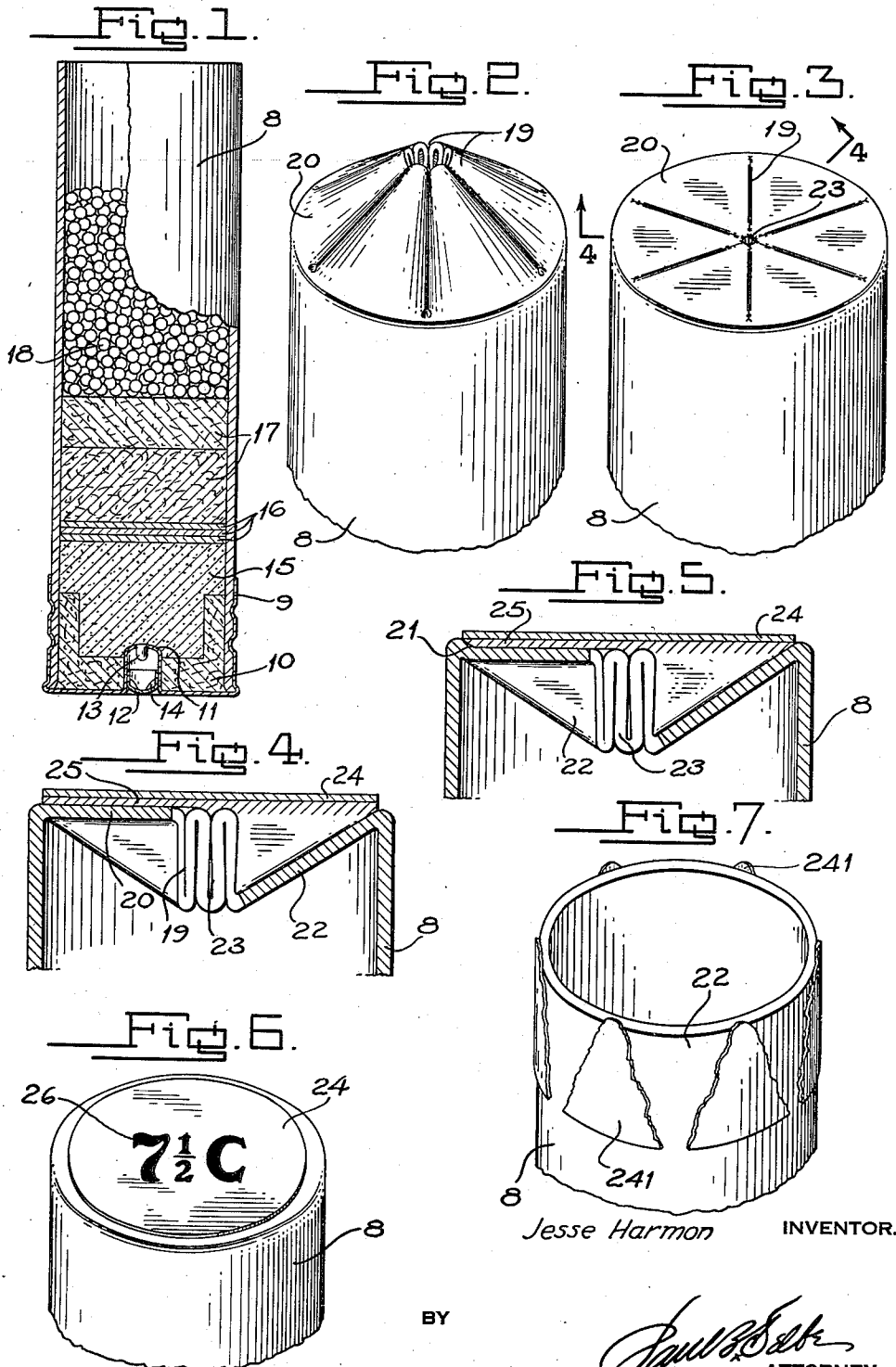
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CLOSURE AND ADHESIVE THEREFOR

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CLOSURE AND ADHESIVE THEREFOR

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This invention relates to shot shells, especially the closing thereof. More particularly, it appertains to the control of firing and ballistics of shot shells having paper or like bodies, by means of body closure seals which are easily applied and which do not cause objectionable barrel fouling.

The shot shell, as generally produced, comprises a fairly rigid paper cylinder (called the "body") having over one end a metal cap (called the "head"). Ordinarily the head contains the propellant powder and means for igniting it. The body contains the shot charge and a partition (filler wad) separating it from the powder. It is universal commercial closing practice to place a card (top wad) over the shot charge and fold the open edge of the body stock inwardly and downwardly (through 180°) to form a bead that rests on top of the wad.

It is self-evident that such a closure has substantially fixed resistance to opening. No part of it can be varied to control pressure or ballistics. This will be even more obvious when it is appreciated that the properties of the body paper are fully determined by considerations other than the closure structure.

This disadvantage cannot be overcome by changing the character of the top wad. Experience has shown that a heavy, hard, unbreakable top wad interferes with the movement of the shot, produces poor patterns, etc., and that fragmentation of a frangible top wad results in a cloud of "confetti-like" beads which tend to obscure the target from the shooter and are blown into his face when the wind is from the general direction of the target. Such arrangements or features are obviously undesirable.

Shot shell bodies are made by rolling a specially prepared porous paper into tube form, the successive layers or convolutions of the paper being secured together by a starch adhesive. For protection against moisture and for other purposes, the rolled tubes are heavily impregnated with a wax, usually paraffin wax, the wax content of the finished tube constituting not less than 20% of the weight of the tube.

Since shot shells must fit rather closely in a gun chamber, the finished bodies must be brought to a given outside diameter with very low tolerances. For this purpose the wax impregnated tubes are passed through a sizing die, which somewhat reduces their outside diameter, and in so doing irons the surface very hard and smooth.

This invention had for objects the utilization of the end portion of the cylindrical tube, which constitutes the body of the shot shell, as the end closure in such a way that (1) the necessity for a separate end closure (top wad) is eliminated; (2) the ballistic properties of the shell are im-

proved; (3) the confinement and burning rate of the propellant powder are accurately controlled; (4) uniformity and improvement are obtained; and (5) loading economies are effected.

Another and more specific object was to provide a body seal which could be varied, coordinated and adapted to the burning characteristics of different propellant powders to more accurately control their confinement and burning rate, and to secure the benefit of the maximum energy available in the combustion thereof without the development of excessive pressures. Still other objects were to seal a shot shell body with material which would not require special preparation of the body surface to receive the same, which would not cause fouling or clogging of the gun barrel even during rapid firing, and which would remain effective during long periods of storage even at temperatures somewhat above those normally encountered in the North Temperate Zone.

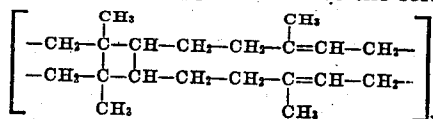
Yet further objects were to close the end of a shot shell with the body material in such a way that "blown patterns" are avoided and patterns better than those resulting from conventional shell closing, are obtained; to coordinate the strength of the body seal with the propellant powder utilized; to provide a closure which would improve the ballistic properties of powders heretofore regarded as inferior or unsuitable; to secure standard velocities with reduced charges of powder and without the production of excessive pressures; and to provide an adhesive for bonding body seal discs to the waxed and ironed body papers which would enable the sealed shell ends to control both pressure and ballistics. A general advance in the art, and other objects which will appear hereinafter, are also contemplated.

The development of an adhesive suitable for use upon shot shell bodies is greatly complicated by the character of the material of these bodies for, as indicated above, in addition to the difficulties of effecting adhesion to a waxed surface (a problem encountered in various arts), the method of manufacture results in a shot shell surface which is not only heavily waxed but, due to the action of the sizing die, is smooth, hard, rigid, non-porous, etc.

It has now been found that by compounding or diluting cyclized rubber with certain amino polymers, there results an adhesive composition which can be used very advantageously to seal the small central unsealed aperture which remains when the end of the shot shell is closed by folding a considerable part of the end portion of the body inwardly, and to influence or govern the opening of the said folded end.

The aforementioned cyclized rubber is a resin-like material obtained when a very high grade of

low protein content rubber is made into a heavy viscous, non-drying cement with benzene, and refluxed with a catalyst such as stannic chloride (U. S. A. Patent No. 2,050,209 to Gehman; also U. S. A. Patents Nos. 1,797,188, 1,846,247, 1,853,334 and 2,052,931). It appears to have the formula:



x being a large whole number somewhat smaller than the number of isoprene units in rubber. Minor variations in certain properties (distortion point, solution viscosity) of the cyclized rubber, obtained by varying the time of reaction (conversion), result in a family of resins offered in commerce under the trade names Pliolite, Plioform, Marbon, etc.

How the foregoing objects and related ends are accomplished will be apparent from the following exposition, in which are disclosed the principle and divers embodiments of the invention, including the best mode contemplated for carrying out the same. Parts are given by weight throughout the application unless otherwise specified.

The written description is amplified by the accompanying drawing, in which:

Figure 1 is an elevation, partly in section, view of a shot shell, primed, loaded and ready for closing;

Figure 2 is a fragmentary perspective view of a shot shell, such as that shown in Figure 1, after it has been subjected to the first or preliminary closing operation;

Figure 3 is a fragmentary perspective view of a fully closed shot shell of the type shown in Figures 1 and 2;

Figures 4 and 5 are fragmentary sectional elevation views taken along intersecting radii (for example, 4-4 in Figure 3) of the closed and sealed end portions of shot shell bodies after the final closing operation, showing the sealing means applied in accordance with this invention;

Figure 6 is a perspective view of that portion of the closed and sealed (finished) shot shell body illustrated in Figure 5; and

Figure 7 is a fragmentary perspective view of the open end of a fired shell having segment-like pieces still adhering thereto.

Similar characters refer to similar parts throughout the drawing.

In the drawing (Figure 1), there is illustrated a conventional shot shell comprising a paper body 8 and a metal head 9. The body is a waxed cardboard tube and the head a brass thimble-like structure. Within the head is a paper base wad 10, a battery cup 11, a primer cup 12, an anvil 13 and a charge of priming composition 14. An "over powder" wad 16 and one or more "filler" wads 17 separate the powder 15 from the shot constituting the charge 18.

When the priming composition is ignited in shells of this type by striking the primer cup with a firing pin, the flame thereof ignites the charge of propellant powder 15, firing the shell.

In the present invention the end of the shot shell is closed by folding in the end portion of the body. This is carried out by first forming in that part of the body above the shot charge, a number of creases 19. As a result the open end of the body is drawn into the frusto-conical form illustrated in Figure 2. It is desirable, but not necessary, that this operation precede the final closing operation in which, in the preferred mode

of operation, the thus partially closed body is subjected to the action of a rotating die of such configuration as to press the segments 20 (between the creases 19) into a plane. This brings about a substantially complete sealing of the body.

Exhaustive tests have shown that it is definitely detrimental to indent the end closure very much, so it is preferred that the flat closure portion be in the plane of the end of the side wall, as illustrated in Figure 4, or only very slightly inset, as shown at 21 in Figure 5. In these two figures, in the interest of clarity the shot charge has not been shown. The creased end portion of the body extends downwardly within the shell, as shown at 22.

When the shell is closed in the manner just described, there remains at the center of the folded in planar end (on the shell axis) an unsealed juncture 23 for which a seal is desirable. To provide such a seal, a disc 24, of paper or similar material as illustrated in Figures 4, 5 and 6, is employed. The principal novelty of this invention is in the composition of the adhesive layer 25, used to secure the sealing disc to the body closure.

It will be obvious that by proper selection (of paper 24) and regulation of adhesive strength of the layer 25, there can be secured any degree of "confinement" of the shell contents (including the propellant powder) up to the limit of the tensile strength of the body material (paper, etc.). An accurate control of ballistics thus becomes possible. Unfortunately, the strength of suitable adhesives decreases with time, so that the aforementioned control of ballistics is dependent upon the discovery of an adhesive which does not begin to weaken for long periods of time (if at all).

An advantage of this invention is illustrated in Figure 6 by the indicia 26. This may indicate the size and character of the shot contained in the shell. Conventional shot shell closures provide no means for accomplishing this purpose.

When the shot shell of this invention is fired, both the adhesive and paper layers (25 and 24) are ruptured as the body straightens to substantially its original cylindrical form. Segment-like portions 241 of the disc 24 remain securely affixed to the body, as shown in Figure 7.

Specific examples of the new adhesive compositions, and shot shells embodying the same, follow.

Example I

A shot shell having a body surface of heavily waxed, very smooth, non-porous paper, was loaded. The open end was then partially closed by creasing and folding inwardly that portion of the body above the shot charge. The partly closed end was then subjected to a rotating die to press the folded material surface into a plane substantially perpendicular to the axis of the shot shell cylinder and containing the end of the side wall, thereby substantially completing the closing of the shell.

Twenty-five (25) parts of isomerized rubber (softening point 55° C.) dissolved in 75 parts of toluene, and 6.2 parts of the resinous reaction product of phenol, formaldehyde and methylamine prepared according to Example I of U. S. A. Patent 2,098,869, dissolved in 6.2 parts of toluene, were mixed until homogeneous. Paper (35 pound sulfite type) slightly heavier than ordinary type-writer paper stock, was coated on one side with the resulting composition, and the solvent re-

moved. The adhesive layer obtained was 0.002 to 0.003 of an inch thick. A disc of suitable size was stamped from the coated paper and secured to the folded end of the shot shell by means of heat and pressure.

Example II

Carry out the sealing of shot shells in the manner described in Example I, with an adhesive prepared from milled cyclized rubber (Pliolite, softening at 30° C.), 25 parts in 75 parts of toluene, and poly-beta-di-methyl-amino-ethyl methacrylate, 6.2 parts, in 6.2 parts toluene. This gives a cyclized rubber to basic resin ratio of 80:20.

Example III

Carry out the sealing of shot shells in the manner described in Example I, with an adhesive prepared from milled cyclized rubber (Pliolite, softening at 30° C.), 25 parts in 75 parts of toluene, and the resinous reaction product of phenol, formaldehyde and methyl amine prepared according to Example I of U. S. A. Patent No. 2,098,869 (Harmon and Meigs), 6.2 parts in 6.2 parts toluene.

Example IV

Carry out the sealing of shot shells in the manner described in Example I, with an adhesive prepared by mixing until homogeneous a solution of 50 parts of milled cyclized rubber (Pliolite having a softening point of 30° C.) in 150 parts of toluene and a solution of 2.6 parts of the resinous reaction product of phenol, formaldehyde and methyl amine (see Example III) dissolved in 5 parts of toluene.

Example V

Carry out the sealing of shot shells in the manner described in Example I, with an adhesive prepared by mixing until homogeneous a solution of 50 parts of milled cyclized rubber (Pliolite softening at 30° C.) in 150 parts of toluene and a solution of 5.5 parts of the resinous reaction product of diphenyl guanidine, formaldehyde and methyl amine (the preparation of which is described elsewhere in the specification under the heading "group F") dissolved in 10 parts of toluene. A cyclized rubber amino resin ratio of 90:10 results.

Example VI

Carry out the sealing of shot shells in the manner described in Example I, with an adhesive prepared by mixing until homogeneous a solution of 40 parts milled cyclized rubber (Pliolite softening at 30° C.) in 120 parts of toluene and a solution of 10 parts of triethanol amine phthalate product (preparation described under group G) in 90 parts of dioxan. The "solids" have a ratio of 80:20.

Example VII

Carry out the sealing of shot shells in the manner described in Example I, with an adhesive prepared by mixing until homogeneous a mixture of a solution of 2.6 parts of diphenyl guanidine formaldehyde resin (preparation described under group E) dissolved in 5 parts of toluene, and a solution of 50 parts of milled cyclized rubber (Pliolite softening at 30° C.) dissolved in 150 parts of toluene. The ratio is 95:5.

Example VIII

Carry out the sealing of shot shells in the

manner described in Example I, with an adhesive prepared by adding 2 parts of n-butyl-diethanolamine-dimethylol urea-dimethyl ether resin (preparation described under group K) dissolved in 20 parts of dioxan to 8 parts of milled cyclized rubber (Pliolite softening at 30° C.) dissolved in 24 parts of toluene.

Example IX

Carry out the sealing of shot shells in the manner described in Example I, with an adhesive prepared by dispersing in 83 parts of toluene by grinding in a ball mill for 18 hours, 16 parts of cyclized rubber (Pliolite softening at 30° C.) and 4 parts of dimethylol urea dimethyl ether-hexamethylene diamine resin (preparation described under group K). The ratio of the components is 4:1.

The adhesive compositions are applied to the sealing paper by conventional means, such as brushes, rollers, doctor knives, etc., after which the solvent is allowed to evaporate. The films thus deposited are non-tacky, waterproof and flexible. They are not adhesive in the dry condition at ordinary temperatures, but when moistened with hydrocarbon solvents such as toluene, or when subjected to heat and pressure, as used in conventional sealing procedures, they have excellent adhesion to materials like the smooth, waxed and ironed cardboard commonly employed for shot shell bodies.

The ratio of cyclized rubber to amino polymer may be varied over a wide range, depending upon the specific adhesive requirements. In general the more amino polymer is used the greater will be the storage life of the adhesive composition, that is to say, the stabilizing effect is roughly proportional to the amount used with the cyclized rubber. Compositions containing as low as 25% of cyclized rubber to 75% of amino polymer, and compositions containing as high as 98% of cyclized rubber and 2% amino polymer, have been found useful. The preferred range is 2%-25% amino polymer and 98%-75% of cyclized rubber. The improvement obtained by using amounts of amino polymer below the aforementioned lower limit is detectable but has not been found to be great enough to be of any practical value.

The cyclized rubber may be prepared in any one of several different ways, and its composition and properties may vary somewhat, but however prepared, it is thermoplastic and less unsaturated than rubber. It appears to have an empirical formula, $(C_5H_8)_x$ and to be a condensation derivative of rubber. The term "condensation" is used in the same sense that it is employed by Cohen (page 245 of his "Organic Chemistry for Advanced Students," 1909 edition), namely:

"Condensation may, then, be defined as the union of two or more organic molecules or parts of the same molecule with or without elimination of component elements, in which the new combination is effected between carbon atoms."

In the condensation, various reagents may be employed for converting rubber into the rubber derivative. In one mode of preparation, a solution (the reaction with the rubber is advantageously carried out in solution) of the rubber in benzene is boiled for an hour or two and then, while continuing the boiling under reflux condenser, up to 10% (based on the amount of rubber) of a conversion agent such as stannic chloride, is added. The heating is then continued for perhaps several hours, until the desired reaction has taken place. The condensation de-

ivative of the rubber is isolated by pouring the reaction mass into water, acetone, alcohol (methyl, ethyl, etc.) and the like.

Tin tetrachloride apparently reacts with the rubber to form a tin chloride addition product of rubber (or cyclized rubber) which probably has the formula $(C_5H_8)_x \cdot SnCl_4$. The tin and chlorine split off upon drowning the reaction product, leaving the cyclized rubber hydrocarbon. In this procedure aluminum chloride, ferric chloride, chromic chloride or another halide of an amphoteric metal, may replace the tin chloride.

Condensation derivatives containing a small amount of combined chlorine are obtained when a rubber cement is treated with chlorostannic acid or a mixture of hydrochloric acid and a compound such as tin tetrachloride. It is not necessary to preboil the cement before treatment if the rubber conversion agent employed is of this sort. In this type of reaction, rubber, milled to a plasticity of about 300, is dissolved in sufficient benzene to form a 10% solution, and to the resultant 10% (based on the weight of the rubber) of crystalline chlorostannic acid is added. The reaction mixture is then heated to boiling under a reflux condenser maintained at or near the boiling point until the desired reaction has taken place.

To isolate the cyclized rubber the reaction mixture is filtered and poured with agitation into sufficient water to form an emulsion in which the solution of the reaction product forms the discontinuous phase. It is advantageous to add a reducing agent such as sodium sulfite to the water to prevent or minimize the oxidation. The emulsion is steam distilled to remove the benzene, with the result that the condensation derivative precipitates as a fine powder.

The deformation point (point at which plastic flow is detectable) of the condensation derivative depends (apparently) upon the extent to which the rubber has been converted to cyclized rubber, that is, the extent to which the conversion agent acts on the rubber. This, in turn, is dependent upon the time and temperature of the treatment. The reaction at the beginning is highly exothermic, and the practical lower limit of conversion is about 25% (the conversion being stopped by drowning the reaction mass promptly). This degree of conversion brings about a deformation point (sometimes called "softening point") of about 30° C. When a conversion of practically 100% has taken place, the deformation point is about 105° C. As will be apparent, the higher the degree of conversion, the higher will be the deformation point.

Products having the lower deformation points are usually obtainable commercially in the non-homogeneous form which results from drowning the reaction mixture and in the uniform condition obtained by milling the non-uniform product. The milled products are generally the more stable of the two and are more uniformly soluble. The distinction between the two types of materials progressively disappears as the degree of conversion approaches completeness. It is advantageous to mill the powder to a homogeneous mass before compounding it with the other ingredients in the present invention, but the unmilled product can be used.

Condensation derivatives with a softening point from 30° to 105° C. are, in general, satisfactory. A product with a softening point around 30° C. is ordinarily employed. Obviously, the most

satisfactory softening point depends upon the particular use to which the material is to be put. Although the 30° C. softening material was employed in many of the specific examples, it is to be understood that any one or a plurality of the products may be employed, when desired.

The cyclized rubber called "Pliolite," mentioned in several of the examples, is a thermoplastic rubber derivative made by condensing rubber with a catalyst of the tin tetrachloride type. Specific details of its preparation, structure, etc., are set forth in the Paper Trade Journal, page 96, February 23, 1939, Rubber Age, April 1939, and J. I. E. C. XIX 1033, XXVI 125 and XXXIII 389.

The amino-nitrogen-containing polymers capable of being formed into coherent films, soluble in organic solvents and in 2% aqueous acetic acid and insoluble in water can for convenience, be divided into sub-groups, as follows:

(A) Resinous polymeric coherent-film-forming reaction products of phenols, aldehydes and material from the group consisting of ammonia, primary amines and secondary amines;

(B) Resinous polymeric coherent-film-forming amino alcohol esters of material from the group consisting of acrylic acid and acrylic acid substituted in the alpha position by a hydrocarbon radical;

(C) Resinous polymeric coherent-film-forming reaction products of amino phenols with aldehydes;

(D) Resinous polymeric coherent-film-forming reaction products of aliphatic ketones (aliphatic and alicyclic) with formaldehyde and material from the group consisting of ammonia, primary amines, secondary amines and tertiary amines;

(E) Resinous polymeric coherent-film-forming reaction products of diaryl (especially diphenyl) guanidine with aldehydes (especially formaldehyde);

(F) Resinous polymeric coherent-film-forming reaction products of diaryl (especially diphenyl) guanidine with aldehydes (especially formaldehyde) and amines (primary or secondary);

(G) Resinous polymeric coherent-film-forming amino alcohol esters of polycarboxylic acids;

(H) Resinous coherent-film-forming aromatic amine aldehyde resins;

(I) Resinous polymeric coherent-film-forming reaction products of vinyl ketone polymers with material from the group consisting of ammonia and amines;

(J) Resinous polymeric coherent-film-forming reaction products of piperazine, aldehydes (especially formaldehyde) and phenols;

(K) Resinous polymeric coherent-film-forming reaction products of dimethylol urea dimethyl ether and amines;

(L) Resinous polymeric coherent-film-forming reaction products prepared by treating polyvinyl chloroacetate with secondary aliphatic amines;

(M) Resinous polymeric coherent-film-forming products resulting from the reaction of urea, formaldehyde, and lower aliphatic (in which the substituent radicals have less than 5 carbon atoms) primary or secondary amines, especially methyl, dimethyl, butyl and dibutyl amines;

(N) Resinous polymeric coherent-film-forming products obtained by polymerizing, in the presence of catalytic proportions of stannic chloride, the reaction product of epichlorohydrin, with material from the group consisting of ammonia and primary aliphatic amines;

(O) Resinous polymeric coherent-film-forming

reaction products of phenol-lignin with dimethyl amine and formaldehyde;

(P) Resinous polymeric coherent-film-forming products obtained by the catalytic hydrogenation of resins having ketone groups at superatmospheric temperature and pressure in the presence of material from the group consisting of ammonia, primary amines and secondary amines; and

(Q) Resinous polymeric coherent-film-forming reaction products of protein material from the group consisting of lower aliphatic aldehydes and lower aliphatic ketones and amines having less than 9 carbon atoms, in which the amino nitrogen is joined to the aliphatic carbon.

These related highly polymeric amino nitrogen-containing substances, which are prepared synthetically, form a distinctive group. Since the corresponding monomers do not accomplish the end desired, it is clear that their effectiveness is dependent upon polymeric form.

Details of the preparation of these basic amino nitrogen-containing polymers are summarized below.

In general, the products of group A are prepared by reacting an aldehyde (preferably formaldehyde) with the appropriate nitrogen compound (ammonia or amine) in aqueous solution to give a methylol derivative (of the ammonia or amine), which is then reacted with the phenol in question. The resin separates from the solution as it is formed, and is usually washed with water before drying. The detailed preparation of these resins is disclosed in the patent literature, see for example, U. S. A. Patent No. 2,098,869 (Harmon and Meigs), particularly Examples A-1, A-7 and A-8, U. S. A. Patent No. 2,168,335 (Heckert), particularly Example A-6, U. S. A. Patent No. 2,168,336 (Heckert), particularly Example A-2, U. S. A. Patent No. 2,031,557 (Bruson) and U. S. A. Patent No. 2,053,092 (Bruson). The preferred combinations are the reaction products of:

	Mols
(1) Phenol	1
Formaldehyde	2
Methylamine	1
(2) Phenol	0.5
Formaldehyde	1.4
Dimethylamine	0.4
Ammonia	0.5
(3) Phenol	1
Formaldehyde	2
Piperazine	1
(4) Beta-naphthol	1
Formaldehyde	2
Methylamine	1
(5) Phenol	1
Formaldehyde	2
N-aminoethyl morpholine	1
(6) Phenol	1
Formaldehyde	2
Ammonia	1
(7) Phenol	1
Formaldehyde	2
Ethylene-diamine	1
(8) Resorcinol	1
Formaldehyde	1
Methylamine	0.5
(9) Diphenylolpropane	1
Formaldehyde	4
Dimethylamine	2
(10) Xylenol	1
Formaldehyde	1.8
Diethanolamine	0.6

In general the polymeric amino nitrogen-containing bodies of group B are prepared by reacting the appropriate amino alcohol with the methyl ester of the acrylic (or alpha-substituted homolog, preferably methacrylic) acid, distilling off the methanol (thereby forming the monomeric amino alcohol acrylate or homolog), and polymerizing (by any suitable means, such as heat, light or peroxide catalyst). The preparation of polymeric esters of this type are disclosed in detail in U. S. A. Patent 2,138,763 (Graves). The polymerization procedures described in U. S. A. Patent 2,138,762 (Harmon) are quite suitable. The preferred esters include poly-(beta-diethyl-aminoethyl-methacrylate), poly-(beta-dimethyl-aminoethyl-methacrylate), poly-4-(beta-methacryloxyethyl)-morpholine, poly-(beta-dicyclohexyl-aminoethyl-methacrylate), triethanolamine-monomethacrylate, and the like.

Preparation of the resins falling in category C is described in detail in U. S. A. Patent 2,147,789 (Graves). The preferred product of this group is that obtained by reacting meta-diethyl-amino-phenol with formaldehyde.

The resinous products of group D are, in general, prepared in the same manner as the preferred material which is the reaction product of acetone, formaldehyde and methyl amine. To prepare this material, a solution of 5 parts of trisodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$) in 50 parts of water was mixed with 50 parts paraformaldehyde. The mixture was cooled in ice, and a solution containing 19 parts (0.61 mol) of methylamine dissolved in 50 parts of acetone, added. A vigorous reaction set in, and cooling was necessary. After the initial reaction was over, the mixture was heated on a steam bath over a reflux condenser for $1\frac{1}{4}$ hours. It was then allowed to stand overnight. A soft brown resinous mass resulted. This was well mixed with water to remove unreacted materials, separated from the water and dried. The final product was an amorphous, orange-colored solid soluble in glacial acetic acid and not precipitated upon dilution of this solution with water. This resin was partially soluble in alcohol, chloroform and dioxan, and was insoluble in acetone, ethyl acetate and toluene.

The resinous products of group E are in general prepared in the same manner as the preferred material which is the reaction product of diphenyl guanidine with formaldehyde. To prepare this material, 43 parts (0.2 mol) of diphenyl guanidine was mixed with 48.6 parts (0.6 mol) of 37% formaldehyde solution, and the mixture allowed to stand with occasional stirring for 18 hours at a temperature of 50°C . The mixture set to a sticky, taffy-like mass which became progressively harder and more brittle. After 18 hours, the resinous mass was ground under cold water, filtered, washed with water and air dried. The final product was a white, amorphous powder soluble in dilute (2%) acetic acid and toluene.

The polymeric basic amino nitrogen-containing bodies of group F are in general prepared in the same manner as the preferred material which is the reaction product of diphenyl guanidine, formaldehyde and methylamine. To prepare this material, a solution of dimethylol methylamine (1 mol) in water was made by passing 31 parts (1 mol) of methylamine into 160 parts (2 mols) of 37% formaldehyde solution cooled with ice. The solution was added to 215 parts (1 mol) of diphenyl guanidine, and the mixture stirred for 15 minutes. This gave a dough-like product

which was allowed to stand for 22 hours to complete the reaction. At the end of this time the mixture became a hard, resinous mass. It was ground under cold water, filtered, washed with water, and dried over calcium chloride in a vacuum desiccator. The reaction product was a white powder soluble in acetone, ethyl acetate, chloroform, dioxan and toluene.

The resinous products of group G are, in general, prepared in the same manner as the preferred material which is the reaction product of triethanol amine and dimethyl phthalate. To prepare this material, a mixture of 149 parts (1 mol) of triethanol amine, 194 parts (1 mol) of dimethyl phthalate and 800 parts of benzene was charged into a reaction flask, and a solution of 2 parts of sodium in 16 parts of methanol was added in small proportions during the course of the reaction as a catalyst. The mixture was heated at a temperature of 130°-155° C. for 9 hours. During this time a binary of methanol and benzene distilled off. When the theoretical amount of binary had been collected in the receiver, the reaction was stopped and the benzene distilled off on a steam bath under reduced pressure. The residue was a viscous oil which, upon cooling, became a soft, resinous mass. The resinous product was soluble in 20% acetic acid, and films flowed from this solution became hard and brittle on baking at 110° C. for 10 hours. The resinous reaction product was soluble in dioxan, 90% ethyl alcohol, 90% acetone and chloroform, and was partly soluble in toluene.

Preparation of the resins falling in category H is described in detail in British Patent 342,325. The preferred reaction product in this group is that from aniline and formaldehyde.

Synthetic resins falling in class I are generally prepared by reacting polymeric vinyl ketones with ammonia or primary amines. The conditions of the reaction and the products are described in detail in U. S. A. Patent No. 2,122,707 (Balthis).

The resinous products of group J are in general prepared in the same manner as the preferred material which is the reaction product of formaldehyde, piperazine and phenol. To prepare this material, 162 parts (2 mols) of aqueous 37% formaldehyde was cooled to 15° C., and 190 parts (1 mol) of piperazine hexahydrate in 200 parts of water added drop-wise at such a rate that the temperature did not rise above 23° C. The reaction vessel was cooled in ice, then 94 parts (1 mol) of phenol in 20 parts of water was added all at once and the ice bath removed. The reaction vessel was then raised to a temperature of 35° C. and allowed to stand over night. A light pink, sticky resin, which was washed with water, was obtained.

The polymeric substances of group K are in general prepared in the same manner as the preferred materials which are the reaction products of dimethylol urea dimethyl ether with n-butyl-diethanol amine and with hexamethylene-diamine.

To prepare the first of these materials, 80.5 parts of n-butyl-diethanol amine and 74 parts of dimethylol urea dimethyl ether were mixed and heated in an atmosphere of nitrogen in a bath maintained at 150°-160° C. for 1.5 hours. Methanol (28 parts) was evolved during this time, and a clear, light-yellow resin, soluble in dioxan, trichlorethylene, dilute aqueous acetic acid and hydrochloric acid, was formed.

To prepare the second of these products, 29

parts of hexamethylene diamine and 37 parts of dimethylol urea dimethyl ether were mixed and gently heated in a distilling vessel in an oil bath until 7 parts of methanol had distilled. The resinous residue in the distilling vessel was washed with water, dissolved in concentrated hydrochloric acid, and precipitated with aqueous sodium hydroxide. The precipitate was filtered, washed with water and dried. A white, amorphous powder, which was soluble in butanol and dilute aqueous acetic acid, was obtained.

The resinous products of group L are prepared, for example, by dissolving 15 parts of di-n-butyl-amine and 10 parts of polymeric vinyl-alpha-chloroacetate in 80 parts of ethylene glycol-monomethyl ether, allowing the solution to stand in a closed vessel for 2 weeks, pouring into 350 parts of water, filtering off the resin which separates, and drying it. The product prepared in the manner just described is an orange-colored rubbery mass soluble in acetone, ethanol and toluene and in 2% aqueous acetic acid. About 13 parts are obtained by this procedure.

The resinous products of group M may be prepared by dissolving two molecular proportions of urea in three molecular proportions of 37% aqueous formaldehyde, adding one molecular proportion of dimethyl (or other alkyl) amino-methanol dissolved in water (50 parts per mol of compound), and heating for about 13 hours. Evaporation of water leaves a white basic resin.

The resinous products of group N are prepared by the procedures described in U. S. A. Patent No. 1,977,251.

The resinous products of group O are prepared by the process of Example B of U. S. A. Patent No. 2,122,433.

The coherent-film-forming resinous products of group P are, in general, prepared in the same manner as the preferred individual polymers whose properties and mode of preparation are described in U. S. A. Patent No. 2,063,153 (Greenewalt).

The amine polymers of group Q are, in general, prepared in the same manner as the preferred species whose properties and mode of preparation are disclosed in U. S. A. Patent No. 2,143,023 (Meigs).

Instead of simple polymers, interpolymers may be prepared, for instance, by reacting methyl methacrylate and methyl vinyl ketone in the presence of ammonium hydroxide or reacting beta - di - cyclohexyl - aminoethyl methacrylate monomer and beta-dimethylaminoethyl methacrylate monomer together under suitable conditions, or reacting dicyclohexylaminoethyl methacrylate with methyl vinyl ketone under suitable conditions. Other equivalent polymeric materials, such as copolymers, may also be used, provided their solubility characteristics are as previously set forth.

The two classes of basic amino-nitrogen-containing polymers which have given the most satisfactory results are the polymeric amino-alcohol esters of alpha-substituted acrylic acids described in U. S. A. Patents 2,138,762 (Harmon) and 2,138,763 (Graves), and the resins obtained by reacting phenols, formaldehyde and amines described in U. S. A. Patent No. 2,098,869 (Harmon and Meigs).

The latter products, which are dilute acetic acid soluble resins, and with which may be classed the very satisfactory phenol formaldehyde piperazine resins, are obtained by reacting a phenol containing carbon, hydrogen and oxygen

only, and having at least 2 unsubstituted nuclear positions ortho or para to the phenolic hydroxyl with formaldehyde and a non-aromatic primary amine containing less than 7 carbon atoms. A molecular ratio of amine to phenol of not less than 0.5:1 and not greater than 1:1, and a molecular ratio of aldehyde to amine not greater than 1:1 in this reaction, give especially desirable results.

The specific compounds which are preferred for the purposes of this invention are beta-di-n-butylaminoethyl methacrylate polymer; 2-amino-cyclohexyl methacrylate polymer; triethanolamine nono-methacrylate polymer; 2-(diethylamino)-cyclohexyl methacrylate polymer; 4-(beta-methacryloxyethyl) morpholine polymer; beta-di-methylaminoethyl methacrylate polymer; beta-diethylaminoethyl acrylate polymer; beta-cyclohexylaminoethyl acrylate polymer; 1-(beta-methacryloxyethyl) piperidine polymer; the resin obtained by the hydrogenation, in the presence of ammonia, of polymerized bis-(4-keto-cyclohexyl) dimethylmethane; the resin obtained from the hydrogenation, in the presence of ammonia, of polymerized methylvinyl ketone; the reaction product of polymeric methyl alpha-methylvinyl ketone and cyclohexylamine; the reaction products of polymeric methylvinyl ketone and aqueous ammonia (or cyclohexylamine, ethylenediamine, hexamethylenediamine, and the like), the resin obtained by reacting cyclohexanone with formaldehyde and methylamine; the resinous reaction product of acetone with formaldehyde and butylamine; and phenol-formaldehyde-hydrazine resin, cresol-formaldehyde-tetraethylenepentamine resin, phenol-formaldehyde-ethylenediamine resin, phenol-formaldehyde-dodecylamine resin, phenol-formaldehyde-thiourea resin and cresol-formaldehyde-melamine resin.

The choice of amino polymer to be used depends partly upon the solubility of the polymer partly on the compatibility of the polymer with the cyclized rubber in solution, and partly on the special requirements of the specific adhesive being manufactured, such as softening point, degree of surface tack, etc. In general, basic resins soluble in toluene or gasoline, compatible with cyclized rubber in solution and capable of imparting the longest possible storage life to the cyclized rubber after the application, are preferred. One criterion of stabilizing power is the basicity of the resin as judged by the per cent of amino nitrogen in the molecule. Usually the higher the percentage of amino nitrogen the longer will be the stabilizing power of the polymer.

Some discussion of the meaning and significance of the terminology describing the stabilizing materials may be desirable. The term "polymeric" implies an amorphous, high molecular weight substance usually capable of being formed into a coherent film. By "basic" is meant an ability to form acid addition salts, and by "amino-nitrogen" is meant the nitrogen of an amino group as opposed to that of nitro, amido, nitrile, etc., groups. It is a matter of simple test to determine if the agent is basic in character and contains amino-nitrogen. In the large majority of cases, the materials from which the agent is synthesized are a definite indication whether or not it contains amino-nitrogen. It is sufficiently basic if it dissolves readily in dilute aqueous acetic acid. The qualification "organic-solvent-soluble" implies simple physical solution (i. e., without chemical reaction) to an appreciable

extent in one or more types of liquids such as alcohols, hydrocarbons, ketones, esters, etc. Thus, methylaminophenol-formaldehyde resin, which is readily soluble in a number of solvents, is suitable for use in the invention, whereas deacetylated chitin is not because it is insoluble in organic solvents.

The polymeric basic amino nitrogen-containing substance may be introduced into the cyclized rubber and compositions containing the same, in any desired manner. Ordinarily the incorporation is made by the use of a mutual solvent or by milling, but grinding, kneading, and other conventional mixing procedures are satisfactory.

The adhesive compositions may be applied to the ammunition parts (paper or other medium) as solutions (used in a broad sense to include both true solutions and pseudo-solutions, which latter are in reality colloidal suspensions), emulsions, melts without any solvent, and melts with reduced amounts of solvent.

The adhesive composition may be applied to the shell body and dried before sealing instead of to the sealing disc, or may be applied to both, as convenience may dictate.

In forming solutions and melts containing small amounts of organic liquids of the cyclized rubber-amino polymer compositions, aliphatic, aromatic and chlorinated hydrocarbons are suitable. The preferred substances are benzene, toluene, xylene, tetrachlorethane, kerosene and related products.

In preparing the adhesive compositions, various adjuvants or augmenting agents, such as resins, plasticizers, waxes, colors, etc., may be incorporated when desired. Variations in proportions of any such conventional modifying ingredients of the stabilized composition are permissible.

The preferred resins (natural, synthetic and semi-synthetic) include rosin, hydrogenated rosin, hydrogenated rosin derivatives, ester gum, pitches, cumarone indene resins, alkyl (polyhydric alcohol-polycarboxylic acid reaction product) resins, damar, and the like. Such materials, individually and in combination, compound readily with the cyclized rubber. Although resins generally improve homogeneity and thermoplasticity, it is not always desirable to have a resin present. When the presence of resins is desirable, one or more may be used.

The preferred plasticizers (sometimes improperly referred to as softeners) are dibutyl phthalate, tricresyl phosphate, chlorinated paraffin, dioxyl ethane, chlorinated diphenyls, hydrogenated methyl abietate, diethyltoluene sulfonamide, camphor, hydrocarbon oils, and the like. One or more of the materials of this character may be present in the adhesive composition, or material of this character may be omitted.

One or more waxes (used generically to include waxy substances like paraffin wax, as well as true waxes which are monohydric alcohol esters of higher fatty acids) may be added to enhance the adhesive and other characteristics of the cyclized rubber-amine polymer compositions, as desired.

The shell bodies and sealing discs may be made of materials other than paper, for example, regenerated cellulose, if desired.

The molecular weight of the amino polymer (basic resin) has some effect on its power to stabilize the cyclized rubber. Resins giving low viscosity solutions at high (50%) solids contents, are preferred. These factors should be taken into consideration in compounding the adhesive, it being desirable, for example, to utilize resinous

materials of high softening point to aid in producing adhesive compositions of high softening points, and vice versa.

Many advantages of the present invention are apparent from the foregoing part of the specification. The bond between the shell body surface (waxed cardboard) and the sealing disc (paper) remains firm at temperatures which are reached at rapid firing (up to 120° F.—49° C.). The adhesive and sealing disc remain firmly secured to the shot shell body after firing, so that no deposit or residue accumulates in the gun barrel. The adhesive composition seals the juncture of the folded closure against the entrance of moisture. The sealing means effects an improvement in pattern, eliminating "blown" patterns (one in which the shot scatters widely). The sealing means characteristics may be correlated with the characteristics of the powder, primer and loaded material to effect loading economies and improved ballistics. The sealing means has thermoplastic characteristics and adheres to the shell material with adequate and controllable tenacity. The adhesive of this invention eliminates the necessity for special treatments of the shot shell body such as abrasion, roughening of the surface, removal of a substantial portion of the waterproofing oil contained in the surface, etc., to facilitate penetration by the adhesive. The adhesives of the present invention do not have objectionably low softening points, and are able to withstand shock. Approximately a 25-fold improvement in adhesive ageing life (at 65° C.) is hereby obtained. The adhesives do not have to be used when freshly prepared.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. In a shot shell, the combination comprising a substantially cylindrical body of wax impregnated deformable material and an exteriorly planar end closure integral with said body and flush with the end thereof, and comprising a plurality of abutting segments and folds joining said segments, said closure including the segments and folds being integral with said body, and a seal for said end closure comprising essentially a thin disc adhesively secured to said end closure by means of milled cyclized rubber diluted with a small amount of basic amino polymer capable of being formed into coherent solid films which are substantially insoluble in water and 5% aqueous ammonia and soluble in 2% aqueous acetic acid and organic solvents.

2. A shot shell body comprising an end closure integral with the side wall thereof, said end closure being sealed with milled cyclized rubber containing 25% resinous reaction product of phenol, formaldehyde and methylamine.

3. A shot shell comprising an integral wax impregnated body, an end closure, and a moistureproofing and ballistic controlling member seal secured to said end closure, said seal comprising essentially a thin disc adhesively secured to said end closure by means of cyclized rubber

having a softening point of 30° C. and containing 2%–75% basic amino polymer capable of being formed into coherent solid films which are substantially insoluble in water and 5% aqueous ammonia and soluble in 2% aqueous acetic acid and organic solvents.

4. A shot shell comprising a body, an end closure integral with said body, and a moistureproofing and ballistic controlling member seal secured to said end closure, said seal comprising essentially a thin disc adhesively secured to said end closure by means of cyclized rubber diluted with a small amount of basic amino polymer capable of being formed into coherent solid films which are substantially insoluble in water and 5% aqueous ammonia and soluble in 2% aqueous acetic acid and organic solvents.

5. In a shot shell, the combination comprising a substantially cylindrical body of wax impregnated deformable material and an exteriorly planar end closure integral with said body and flush with the end thereof, and comprising a plurality of abutting segments and folds joining said segments, said closure including the segments and folds being integral with said body, and a seal for said end closure comprising essentially a thin disc adhesively secured to said end closure by means of cyclized rubber containing 2%–75% basic amino polymer capable of being formed into coherent solid films which are substantially insoluble in water and 5% aqueous ammonia and soluble in 2% aqueous acetic acid and organic solvents.

6. In a shot shell, the combination comprising a substantially cylindrical body of wax impregnated deformable material and an exteriorly planar end closure integral with said body and flush with the end thereof, and comprising a plurality of abutting segments and folds joining said segments, said closure including the segments and folds being integral with said body, and a seal for said end closure comprising essentially a thin disc adhesively secured to said end closure by means of unmilled cyclized rubber containing 25% resinous reaction product of phenol, formaldehyde and methylamine.

7. A shot shell body comprising an end closure integral with the side wall thereof, said end closure being sealed with milled cyclized rubber containing 25% resinous reaction product of phenol, aldehyde and amine.

8. In a shot shell, the combination comprising a substantially cylindrical body of wax impregnated deformable smooth cardboard and an exteriorly planar end closure integral with said body and flush with the end thereof, and comprising a plurality of abutting segments and folds joining said segments, said closure including the segments and folds being integral with said body, and a seal for said end closure comprising essentially a thin 35 pound sulfite paper disc adhesively secured to said end closure by means of cyclized rubber product diluted with a small amount of basic amino polymer capable of being formed into coherent solid films which are substantially insoluble in water and 5% aqueous ammonia and soluble in 2% aqueous acetic acid and organic solvents.

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