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REACTION MIXTURE OF FORMALDEHYDE-HYDRAZIDE-TRIAZONE FOR TREATING CELLULOSIC TEXTILES

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This invention relates to the treatment of cellulosic textiles to impart wrinkle resistance to the textile. More particularly it relates to the impregnation of cellulosic textiles with solutions containing formaldehyde and the products of its reaction with a hydrazide and a tetrahydro-S-triazone.

The use of hydrazide-formaldehyde reaction product to impart wrinkle resistance to textiles has been briefly described in U.S. 2,161,808. The latter generally implies that resistance to creasing and crushing of textiles can be improved by impregnating them with reaction products of hydroxylamine or hydrazine or derivatives of these bodies with formaldehyde or other aldehydes or substances yielding or acting as aldehydes. The process involves dipping the textile in an aqueous solution of the hydroxylamine or hydrazide derivative, drying the textile, impregnating it with an aldehyde and finally curing the textile by heating. It has been experimentally determined that while the treatment of textiles as described in U.S. 2,161,808 does impart some crease resistance to cellulosic textiles, however, the product has several disadvantages which render it noncompetitive with those produced by current processes. The most serious drawbacks are an inferior crease resistance and a large loss in the tensile strength of the textile.

The use of polymethylol hydrazides of dibasic acids as antiwrinkling or crease-proofing agents for cellulosic textiles is described in pending applications Serial Numbers 731,146 and 731,147, filed April 28, 1958, of Robert L. Holbrook and Richard L. Doerr, now U.S. Patents 2,904,387 and 2,904,388, respectively. These applications describe the preparation of the polymethylol hydrazides of dibasic acids, by reaction of formaldehyde and dihydrazides of dibasic acids, and their application to cellulosic textiles. The finishes produced are superior to any in general commercial use with respect to durable wrinkle resistance and absence of chlorine retention upon bleaching, two of the most important properties of an antiwrinkling agent. In co-pending application Serial No. 731,146, now U.S. Patent 2,904,387, a series of compositions based on hydrazides of alkylene dibasic acids are described. Those crease-proofing agents are reaction products of formaldehyde (including convenient sources thereof such as paraformaldehyde) and dihydrazides of the general formula $R(CONHNH_2)_2$, wherein R is $(—CH_2—)_n$, wherein n is 0 to 5, or mixtures of such dihydrazides, for example oxalic, malonic, succinic, glutaric, adipic and pimelic. The creaseproofing agents of Serial No. 731,147, now U.S. Patent 2,904,388, are reaction products of formaldehyde (including conventional sources thereof such as paraformaldehyde) and dihydrazides of the general formula $R(CONHNH_2)_2$, wherein R is a saturated chain of 2 to 6 carbon atoms and is interrupted by one or two oxygen or sulfur atoms in the form of ether or thioether linkages, for example diglycolic acid, thiodiglycollic acid,

$$HOOC—CH_2O—CH_2—CH_2—OCH_2—COOH$$

and the like, or mixtures of such dihydrazides.

In addition, co-pending application of Holbrook and Doerr, Serial No. 779,058, filed December 9, 1958, now

U.S. Patent 2,904,390, describes creaseproofing compositions for cellulosic textiles derived from formaldehyde (or convenient sources thereof such as paraformaldehyde) with a hydrazide of a monocarboxylic acid having the formula RCONHNHR' wherein R is H or an alkyl or substituted alkyl group and R' is H or



The R of the formula and the R of the R' group can be the same or different. Preferably, the alkyl group contains from 1 to 8 carbon atoms and the substituted alkyl group is substituted by hydroxyl or sulfhydryl groups. Examples of preferred monohydrazides include diformic hydrazide, acetic hydrazide, diacetic hydrazide, glycolic hydrazide, thioglycollic hydrazide, propionic hydrazide, and gluconic hydrazide.

It has now been found that particularly advantageous creaseproofing results are obtained when any of the monohydrazides or dihydrazides described in the previously filed Holbrook and Doerr applications are combined with formaldehyde and a tetrahydro-S-triazone to form polymethylol derivatives for creaseproofing. The solutions of the invention containing this particular combination of ingredients impart to textiles the outstanding advantages of combining a high degree of resistance to creasing (measured by crease angle as described in the examples), a high retention of tensile strength and tear strength, a high "wash and wear" drip dry rating, low chlorine retention and high resistance to copper pick-up. The solutions are particularly valuable in the treatment of cellulosic textile materials such as textiles fabricated from natural cellulose, e.g. cotton and linen, and regenerated cellulose, e.g. viscose and cuprammonium rayon.

The compositions of the invention are aqueous solutions containing formaldehyde, a monohydrazide or dihydrazide reaction product with formaldehyde and a triazone-formaldehyde reaction product. This invention includes concentrates containing formaldehyde and the above reaction products with as little as 25% by weight of water as well as the pad baths obtained by diluting such concentrates with water and adding the catalyst. The preferred pad baths contain the following proportions of ingredients:

(1) Formaldehyde	moles	1–20
(2) Triazone and/or substituted triazone reaction product with CH_2O	moles	0.5–8
(3) Monohydrazide and/or dihydrazide reaction product with CH_2O	moles	1
(4) Water, percent by weight based on entire composition	percent	70–95
(5) Catalyst, percent by weight based on entire composition	percent	0.2–5

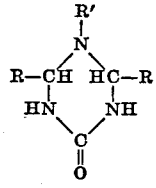
Other proportions of ingredients can be made to function satisfactorily, however, the best results are obtained using the above ratios. It is not exactly known how much of the formaldehyde is reacted with the hydrazide and the triazone, however, there should be excess formaldehyde present. Theoretically, every hydrogen atom attached to a nitrogen atom is reactable with a formaldehyde molecule to form the methylol group. Thus a hydrazide group (—$CONHNH_2$) can react with 3 molecules of formaldehyde and one mole of the dihydrazides described above can theoretically consume 6 moles of formaldehyde. The triazones can react with 2 moles of formaldehyde if substituted in the 5-position and three moles if unsubstituted. As indicated by the above table, mixtures of hydrazides and mixtures of triazones are suitable.

The preferred method of operation by this invention comprises preparing the hydrazide-formaldehyde reac-

tion product containing excess formaldehyde, preparing the triazone-formaldehyde reaction product containing excess formaldehyde and blending these two solutions to form a concentrate which can be handled and shipped in this form. Prior to its use, it is diluted with water and the catalyst is added.

The hydrazide-formaldehyde reaction product is best prepared by slowly adding the hydrazide to aqueous formaldehyde with stirring and cooling to maintain the temperature below about 40° C., e.g. about 10 to below about 40° C. When a monohydrazide is used the ratio of the latter to the formaldehyde should be about 1 mole of hydrazide to between about 3 and 10 moles of formaldehyde. The reaction goes smoothly at an alkaline pH. It is preferable to maintain the pH at about 7 to 10, preferably 7 to 9, during the formaldehyde-monohydrazide reaction to avoid the formation of any resinous product—this can be done by the incremental addition of a dilute base, e.g. sodium hydroxide. When a dihydrazide is used the mole ratio should be about 6 to 20 moles of formaldehyde per mole of the dihydrazide. Also, when reacting a dihydrazide with formaldehyde, care should be taken not to allow the pH to become acid during the addition period as solid products may form. This is easily done by dropwise addition of a dilute base such as sodium hydroxide or sodium carbonate. Very little is required. Preferably, the pH is maintained at about 6 to 11, preferably about 7.5 to 9.5. The water present should come to about 40 percent to 70 percent by weight of the final composition.

The tetrahydro-S-triazones useful in this invention are those of the formula



wherein R and R′ are the same or different and are hydrogen, alkyl radicals of 1 to 5 carbon atoms or hydroxyalkyl radicals of 1 to 5 carbon atoms. Tetrahydro-S-triazone $OC(NHCH_2)_2NH$, tetrahydro-5-ethyl-S-triazone $OC(NHCH_2)_2NC_2H_5$, and tetrahydro-5-beta-hydroxyethyl-S-triazone $OC(NHCH_2)_2NCH_2CH_2OH$, are especially useful.

The triazone or substituted triazone-formaldehyde reaction product can be prepared in several ways; however, it is preferable to prepare the triazone or substituted triazone from urea and ammonia or an amine in the presence of aqueous formaldehyde. Better results are obtained than when the preformed triazone is reacted with aqueous formaldehyde with or without the presence of a hydrazide. Accordingly, equimolar quantities of urea and either ammonia and/or an amine are dissolved in water. If ammonia is used, the product will be unsubstituted triazone, but if an amine is used the substituent thereon will appear in the triazone, at the 5-position, i.e.

$$RNH_2+2CH_2O+CO(NH_2)_2\rightarrow CO(NHCH_2)_2NR+2H_2O$$

Next the formaldehyde, preferably paraformaldehyde, is slowly added while agitating and cooling the mixture to maintain its temperature below about 70° C. After all of the formaldehyde is in, the solution is refluxed (90°–100° C.) for about ¾ to 1½ hours and then allowed to cool to room temperature. It is then ready to be mixed with the hydrazide solution and diluted for use. The proportions of ingredients selected in the above preparation are:

Urea	moles	1
Ammonia or amine	do	1
Formaldehyde	moles	4–10
Water	percent by weight	15–50

After the polymethylol hydrazide and polymethylol thiazone solutions are prepared they are mixed to form the concentrate of this invention or they can be mixed and diluted or diluted and mixed to form the pad bath containing 70% to 95% by weight of water. An alternative method for preparing the concentrate comprises reacting the hydrazide and formaldehyde by mixing the hydrazide with a solution containing the triazone-formaldehyde reaction product and enough excess formaldehyde to form the concentrate described above. If desired, a water solution alcohol, methanol preferred, can be added to the concentrate up to 50% by weight to stabilize it against precipitation of solids during prolonged storage.

The addition of certain catalysts to the polymethylol solution is desirable before use in treating cloth in order to make the treatment more durable to laundering. It is a further feature of the present invention to provide new catalyst compositions which give the most advantageous results with the mixed hydrazide-triazone polymethylol products. The new catalysts comprise a mixture of magnesium chloride and a dibasic organic acid which is either citric or maleic acid or mixtures thereof. The relative proportion of magnesium chloride to the dibasic organic acid is from about 75:25 to 25:75 by weight prepared in an aqueous solution containing from 20 to 40 percent by weight of total solids, the balance being water. This solution is added to the pad bath to the extent that it contains 0.2 percent to 5.0 percent by weight of solid catalyst based on the weight of the pad bath. The catalyzed solution is then ready to be applied to cellulosic textiles.

In accordance with the invention, a solution or diluted concentrate prepared as described above is padded onto the cloth, in the usual manner and preferably while the padding bath has a pH from about 2 to about 5, to the extent that the dry pick-up or add-on, after the cloth is cured, is between about 2 percent and 15 percent by weight, based on the weight of the dry cloth. This add-on is generally accomplished by a wet pick-up of about 65 to 85 percent with the baths described above. An add-on or dry pick-up of over 15 percent is required with certain cloths such as linen, however, there is generally insufficient added advantage to justify this with cotton or rayon.

The curing step, i.e., the reaction of the formaldehyde-hydrazide adduct with the textile, is carried out by standard procedure. Thus, the wet textile is subjected to an elevated temperature until dry and then further heated to effect the curing. Complete cure can be obtained by heating at 150 to 200° C. for ½ to 10 minutes. The curing period is temperature dependent and can be varied over a wide range. Thus, complete curing can also be attained in 15 to 60 seconds at temperatures above 200° C. After the cloth has been cured, it is finished according to standard textile mill procedure. An alkaline scour generally follows the crease-proofing process to remove any excess, unreacted creaseproofing agent and to improve the hand, or feel of the cloth. Normal finishing operations can include calendering, framing, blueing, compressive shrinking, etc.

Example I

A stock solution was made up having the following proportions of ingredients:

Diglycolic dihydrazide	mole	1
Formaldehyde	do	12
Water	percent by wt	43
Methanol	do	17

The solution was prepared by slowly adding the diglycolic hydrazide to aqueous formaldehyde, containing a minor amount of methanol, with stirring while maintaining the temperature of the mixture at about 35° C. by cooling. The pH of the mixture was maintained about 8 by means of dilute caustic adition. After the mixing was complete

the dihydrazide-formaldehyde reaction product was formed. Finally, methanol was added to the proportion shown.

A second stock solution was prepared by reacting ethylamine, urea and paraformaldehyde in mole ratios of one mole of ethylamine, one mole of urea and four moles of formaldehyde. After the reaction was completed by refluxing the reactants in an 18 percent aqueous solution at 90°–97° for about 70 minutes, enough formaldehyde was added to the aqueous solution to the extent of 2 moles of formaldehyde per mole of triazone contained therein. Water was then added to the extent that its final proportion was 35% by weight.

The two solutions were mixed in different ratios. The table below indicates the final proportions of ingredients. Up to 6 moles of the formaldehyde in solutions A, B and C are reacted with the diglycolic acid, however this is not shown by the table because the exact composition of this reaction product is not known.

	A	B	C	D
Diglycolic dihydrazide (moles)	1.0	1.0	1.0	------
Formaldehyde (moles)	12	14	16	1.3
Ethyltriazone·2CH_2O (moles)	------	1.6	3.7	1.2
Methanol (grams)	235	235	235	------
Water (grams)	553	750	998	144
Percent active ingredients	40	47	52	65
Use level, 7%				
Cure time, 4 min.				
Cure temp., 340° F.				
Catalyst, 0.3–0.6%.				
Crease angle (degrees)	128	130	126	128
Tensile strength (pounds) after bleaching (AATCC 69-52)	15	17	21	17

The effectiveness of each of the above solutions as creaseproofers was tested by diluting each of them with water to contain about 90% thereof. A catalyst comprising 35% by weight of maleic acid and 65% of magnesium chloride was added to the diluted baths to the extent of about 0.3 to 0.6 percent by weight. Four cuts of white cotton broadcloth having a thread count of 136 x 64 and weighing about 0.3 pound per square yard were impregnated with the diluted solutions to the extent that the cloths increased in weight by 7 percent after they were dried. They were then cured by heating at 340° F. for 4 minutes. After curing, the cloths were washed, scoured and conditioned for the wrinkle recovery test by storing them in an atmosphere of 65 percent relative humidity and 70° F. for 24 hours. The crease angle reported in the above table was then obtained by folding a strip of cloth in half and pressing it with a 500 gram weight for 5 minutes. The value in the table indicates the angle to which the cloth opens when the weight is removed—AATCC Tentative Test Method 66–53. A sample of untreated cloth has a crease angle of about 65°. In order to determine the susceptibility of the treated cloths to damage by chlorine retention, they were bleached in a dilute sodium hypochlorite solution. After bleaching, the cloths were scorched by a hot iron to effect the fiber damage caused by the chlorine retention. The table indicates that mixture C produced cloth which was 24 percent stronger than that obtained by the straight triazone treatment, D. The mixture B produced a cloth which was 13 percent stronger than did the unblended diglycolic hydrazide preparation, A. The mixture B is superior to D in that it produced a higher crease angle at an equivalent tensile strength. The latter two properties are roughly inversely proportional to each other, i.e. the higher the crease resistance the more damaged the cloth.

Example II

An aqueous pad bath was made up by mixing the stock solutions of Example I to contain 1.37 percent of diglycolic dihydrazide, 3.03 percent formaldehyde, some of which

is reacted with the hydrazide, 4.4 percent of ethyltriazone·2 formaldehyde composition, 90.48 percent water, 0.36 percent maleic acid and 0.36 percent magnesium chloride. The water and catalyst were added after the stock solutions were mixed.

White cotton cloth having a thread count of 64 x 60 and running 2.52 yards per pound was padded by passing through the bath with a pick-up of 75 percent of the solution. The cloth was run over a dry can at about 90° C. and then cured for 80 seconds at 330° F. After the curing step the cloth was scoured and rinsed.

Samples of the cloth taken at intervals during the run were pressed with an iron until almost dry and placed in a constant humidity and temperature room (60 percent relative and 72° F.) for 24 hours before testing. The crease angle was determined by AATCC Tentative Test Method 66–53. The tensile strength was determined by means of a Scott tensile tester, recording the results as the number of pounds required to pull apart a strip of cloth one inch wide. The tear strength was measured by the tongue method employing a Scott tensile tester. The wash and wear, drip dry rating was measured after machine washing and drip drying, using the Monsanto standards (AATCC 88–1958).

In these tests the crease angle of the various samples averaged 137°. The tensile strength of the weaker fiber was 29. The tear strength was 2.5 pounds and the wash and wear, drip dry rating was 3.0.

Example III

An aqueous pad bath was made up by mixing the stock solutions of Example I to contain 2.0 percent by weight of diglycolic dihydrazide, 2.4 percent of formaldehyde some of which is reacted with the hydrazide, 4.4 percent of ethyltriazone·2 formaldehyde composition, 90.48 percent water, 0.36 percent maleic anhydride and 0.36 percent of magnesium chloride hexahydrate. The water and catalyst were added after the stock solutions were mixed.

White cotton broadcloth having a thread count of 136 x 64 and running 3.22 yards per pound was treated as described in Example II. Upon testing the values were found to be: crease angle 136°, tensile strength of weak fiber 30.2 pounds, the wash and wear rating was 3.0 and the tear strength was 1.3 pounds.

Example IV

Six pad solutions were made up each containing the following proportions of ingredients.

	Parts by weight	Molar ratios
Ethyltriazone·2CH_2O	27.5	3.8
Diglycolic dihydrazide	6.2	1.0
CH_2O	19.3	16
H_2O	650	------
Catalyst	4.2	------

This was accomplished by adding a reacted concentrate of 2 moles of formaldehyde per mole of ethyltriazone containing a slight excess of formaldehyde to a concentrate containing 12 moles of formaldehyde per mole of diglycolic hydrazide. To 100 parts by weight of the resulting concentrate there was added about 600 parts by weight of water to bring its proportion to about 93% by weight.

The catalyst comprised a different ratio of maleic acid to magnesium chloride in each of the six pad baths. These solutions were padded on six separate pieces of cotton broadcloth, the cloths were dried and cured at 360° F. for 4 minutes and their crease angles and tensile strengths were measured. The untreated cloth had original values of about a 50 pound tensile strength and 65° crease angle.

The treated cloth's values are listed in the following table:

[Weight ratio of maleic acid to magnesium chloride in catalyst]

	0/100	25/75	50/50	75/25	90/100	100/0
Crease angle, degrees	125	134	134	132	125	107
Tensile strength	28	28	26	28	33	32

Example V

A reacted solution containing 55 percent by weight of ethyltriazone·2 formaldehyde, 35 percent by weight of water and 10 percent by weight of formaldehyde was mixed with an aqueous solution containing 40 percent by weight of acetic hydrazide and formaldehyde in a mole ratio of 1 to 6 which was prepared by simply admixing the components. The solutions were mixed in a ratio of 4 parts by weight of the former to 5 parts by weight of the latter. After dilution with water and addition of catalyst the pad bath had the following composition:

Ethyltriazone·$2CH_2O$	moles	1.4
Acetic hydrazide [1]	do	1.0
CH_2O	do	7.4
H_2O	percent by weight	90.4
Maleic acid	do	0.45
Magnesium chloride	do	0.15

[1] The hydrazide is actually a polymethylol derivative, being reacted with some of the formaldehyde.

The solution described above was padded onto white cotton broadcloth having a thread count of 136 x 64 and running 3.3 yards per pound, to the extend that the cloth increased in weight by 7 percent after it was dried and then cured at 360° F. for 4 minutes. After scouring the treated cloth and conditioning it in air at 65 percent relative humidity and 70° F. for 24 hours the important characteristics were:

	Treated	Original
Crease angle, degrees	129	65
Tensile strength, pounds	32	55
Wash and wear rating	3.5	1

The tensile strength of the treated cloth was 30 pounds after bleaching and scorching, indicating that there is substantially no chlorine retention by the resin.

Example VI

A rayon taffeta was treated with a solution containing the following ingredients:

58 percent by weight of a formaldehyde-diglycolic dihydrazide solution prepared as in the first paragraph of Example 1.

24 percent by weight of a tetrahydro-5-hydroxyethyl-S-triazone·2 formaldehyde solution prepared as described in the second paragraph of Example 1, except that hydroxyethylamine was substituted for the ethylamine.

18 percent by weight of water.

The concentrate prepared in this manner was diluted with water until the proportion of water therein was about 92 percent by weight. To this diluted pad bath there was added 0.9 percent by weight of citric acid and 0.6 percent by weight of magnesium chloride as mixed catalysts, and about 2 percent by weight of a polyethylene emulsion which acted as a softener for the cloth.

The rayon taffeta was passed through the bath, dried and cured by heating it at 360° F. for 4 minutes. After cooling, it was placed in an atmosphere of 65% relative humidity and 70° F. for 24 hours to standardize it for crease angle determination. The increase in weight of the cloth due to the added creaseproofer was about 6 percent. The crease angle of this treated rayon was 133° compared to its original value of 92°, while at the same time the tensile strength dropped only 5 pounds from an original value of 50 pounds.

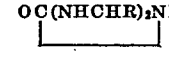
Example VII

A concentrate was prepared by adding 16 grams of diglycolic dihydrazide with stirring to 120 grams of 30 percent by weight aqueous formaldehyde. During the addition the pH of the mixture was maintained slightly alkaline by the addition of small amounts of dilute sodium hydroxide. To this solution there was added 59 grams of a solution containing 20 grams of water, 33 grams of dimethylol ethyltriazone and 6 grams of formaldehyde. Finally, 37 grams of water was added and the concentrate was stirred to make it a homogeneous solution.

Several cuttings of mercerized linen, having a thread count of about 36 by 36 per inch, were padded with a solution prepared by diluting 100 grams of the above concentrate with 200 grams of water and dissolving 10 grams of $MgCl_2 \cdot 6H_2O$ as catalyst therein. After roller-ringing the cloths they had an average wet pick-up equal to 80 percent of their initial dry weight. The cloths were dried and then cured at about 320° F. for 3 minutes, scoured with soap and soda ash solution at 180° F., washed with water, bleached with hydrogen peroxide, soured with 5 percent acetic acid, rinsed and finally dried. The crease angles were measured by the Tootal-Broadhurst-Lee method (Textile Research Journal 19–234–5 (1949)). The values averaged about 3.3 centimeters in contrast to only 1.6 centimeters prior to the treatment.

What is claimed is:

1. A composition useful in the impregnation of a textile, fabricated from a material selected from the group consisting of cellulose and regenerated cellulose, to render it resistant to wrinkling and creasing consisting essentially of an aqueous solution containing the ingredients (1) formaldehyde; (2) the reaction product of formaldehyde and a triazone of the formula



wherein R and R′ are selected from the group consisting of hydrogen, alkyl of 1 to 5 carbon atoms and hydroxyalkyl of 1 to 5 carbon atoms; and (3) a formaldehyde-hydrazide reaction product selected from the group consisting of (*a*) the reaction product of formaldehyde and a monohydrazide produced by the reaction of a monohydrazide, of the formula

$$RCONHNHR'$$

wherein R is selected from the group consisting of hydrogen, alkyl of 1 to 8 carbon atoms and alkyl of 1 to 8 carbon atoms substituted by one of the groups hydroxyl and sulfhydryl and R′ is selected from the group consisting of hydrogen and



and formaldehyde in a molar ratio of formaldehyde to the hydrazide of about 3:1 to 10:1, and (b) the reaction product of formaldehyde and a dihydrazide produced by the reaction of a dihydrazide, of the formula

$$R(CONHNH_2)_2$$

wherein R is selected from the group consisting of $(—CH_2—)_n$ wherein *n* is an integer having a value of 0 to 5 and alkylene of 2 to 6 carbon atoms interrupted by from 1 to 2 atoms selected from the group consisting of oxygen and sulfur, and formaldehyde in a molar ratio of formaldehyde to the dihydrazide of about 6:1 to 20:1, the total amount of said ingredients in the solution being from 5 to 75 weight percent and the proportions of said ingredients in the solution being about 1 to 20 moles of

formaldehyde, about 0.5 to 8 moles of the formaldehyde-triazone reaction product and about 1 mole of the formaldehyde-hydrazide reaction product.

2. The composition of claim 1 which also contains about 0.2 to 5 weight percent of a catalytic mixture consisting essentially of a mixture of magnesium chloride and a dibasic organic acid selected from the group consisting of citric acid, maleic acid and mixtures thereof.

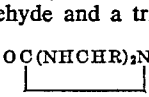
3. The composition of claim 1 which also contains about 0.2 to 5 weight percent of catalytic mixture consisting essentially of a mixture of magnesium chloride and a dibasic organic acid selected from the group consisting of citric acid, maleic acid and mixtures thereof, the proportion of magnesium chloride to dibasic acid being about 75:25 to 25:75 parts by weight.

4. A composition useful in the impregnation of a textile, fabricated from a material selected from the group consisting of cellulose and regenerated cellulose, to render it resistant to wrinkling and creasing consisting essentially of an aqueous solution containing the ingredients (1) formaldehyde, (2) the reaction product of tetrahydro-5-ethyl-S-triazone and formaldehyde, and (3) the reaction product of formaldehyde and diglycolic dihydrazide in a molar ratio of formaldehyde to the dihydrazide of about 6:1 to 20:1; the total amount of said ingredients in the solution being from about 5 to 75 weight percent and the proportions of said ingredients in the solution being about 1 to 20 moles of formaldehyde, about 0.5 to 8 moles of the formaldehyde-triazone reaction product and about 1 mole of the formaldehyde-hydrazide reaction product.

5. A composition useful in the impregnation of a textile, fabricated from a material selected from the group consisting of cellulose and regenerated cellulose, to render it resistant to wrinkling and creasing consisting essentially of an aqueous solution containing the ingredients (1) formaldehyde, (2) the reaction product of tetrahydro-5-ethyl-S-triazone and formaldehyde, and (3) the reaction product of formaldehyde and acetic hydrazide in a molar ratio of formaldehyde to the hydrazide of about 3:1 to 10:1; the total amount of said ingredients in the solution being from about 5 to 75 weight percent and the proportions of said ingredients in the solution being about 1 to 20 moles of formaldehyde, about 0.5 to 8 moles of the formaldehyde-triazone reaction product and about 1 mole of the formaldehyde-hydrazide reaction product.

6. A composition useful in the impregnation of a textile, fabricated from a material selected from the group consisting of cellulose and regenerated cellulose, to render it resistant to wrinkling and creasing consisting essentially of an aqueous solution containing the ingredients (1) formaldehyde, (2) the reaction product of tetrahydro-5-beta-hydroxyethyl-S-triazone and formaldehyde, and (3) the reaction product of formaldehyde and diglycolic dihydrazide in a molar ratio of formaldehyde to the dihydrazide of about 6:1 to 20:1; the total amount of said ingredients in the solution being from about 5 to 75 weight percent and the proportions of said ingredients in the solution being about 1 to 20 moles of formaldehyde, about 0.5 to 8 moles of the formaldehyde-triazone reaction product and about 1 mole of the formaldehyde-hydrazide reaction product.

7. A method for the impregnation of a textile, fabricated from a material selected from the group consisting of cellulose and regenerated cellulose, to render it resistant to wrinkling and creasing which includes the steps of impregnating the textile with an aqueous solution containing the ingredients (1) formaldehyde; (2) the reaction product of formaldehyde and a triazone of the formula



wherein R and R′ are selected from the group consisting of hydrogen, alkyl of 1 to 5 carbon atoms and hydroxyalkyl of 1 to 5 carbon atoms; and (3) a formaldehyde-hydrazide reaction product selected from the group consisting of (*a*) the reaction product of formaldehyde and a monohydrazide produced by the reaction of a monohydrazide, of the formula

$$RCONHNHR'$$

wherein R is selected from the group consisting of hydrogen, alkyl of 1 to 8 carbon atoms and alkyl of 1 to 8 carbon atoms substituted by one of the groups hydroxyl and sulfhydryl and R′ is selected from the group consisting of hydrogen and



and formaldehyde in a molar ratio of formaldehyde to hydrazide of about 3:1 to 10:1, and (*b*) the reaction product of formaldehyde and a dihydrazide produced by the reaction of a dihydrazide, of the formula

$$R(CONHNH_2)_2$$

wherein R is selected from the group consisting of $(—CH_2—)_n$ wherein *n* is an integer having a value of 0 to 5 and alkylene of 2 to 6 carbon atoms interrupted by from 1 to 2 atoms selected from the group consisting of oxygen and sulfur, and formaldehyde in a molar ratio of formaldehyde to the dihydrazide of about 6:1 to 20:1; the total amount of said ingredients in the solution being at least 5 weight percent and the proportions of the ingredients in the solution being about 1 to 20 moles of formaldehyde, about 0.5 to 8 moles of the formaldehyde-triazone reaction product and about 1 mole of the formaldehyde-hydrazide reaction product; and heating the impregnated textile to dry it and provide a textile resistant to creasing and wrinkling.

8. The method of claim 7 in which the aqueous solution also contains about 0.2 to 5 weight percent of a catalytic mixture comprising a mixture of magnesium chloride and a dibasic organic acid selected from the group consisting of citric acid, maleic acid and mixtures thereof.

9. The method of claim 7 in which the aqueous solution also contains about 0.2 to 5 weight percent of a catalytic mixture comprising a mixture of magnesium chloride and a dibasic organic acid selected from the group consisting of citric acid, maleic acid and mixtures thereof, the proportion of magnesium chloride to dibasic acid being about 75:25 to 25:75 parts by weight.

10. The method of claim 7 wherein said textile is cotton.

11. A method for the impregnation of a textile, fabricated from a material selected from the group consisting of cellulose and regenerated cellulose, to render it resistant to wrinkling and creasing which includes the steps of impregnating the textile with an aqueous solution containing the ingredients (1) formaldehyde, (2) the reaction product of tetrahydro-5-ethyl-S-triazone and formaldehyde, and (3) the reaction product of formaldehyde and diglycolic dihydrazide in a molar ratio of formaldehyde to the dihydrazide of about 6:1 to 20:1; the total amount of said ingredients in the solution being at least about 5 weight percent and the proportions of said ingredients being about 1 to 20 moles of formaldehyde, about 0.5 to 8 moles of the formaldehyde-triazone reaction product and about 1 mole of the formaldehyde-hydrazide reaction product; and heating the impregnated textile to dry it and provide a textile resistant to creasing and wrinkling.

12. The method of claim 11 in which the aqueous solution also contains about 0.2 to 5 weight percent of a catalytic mixture comprising a mixture of magnesium chloride and maleic acid.

13. A method for the impregnation of a textile, fabricated from a material selected from the group consisting of cellulose and regenerated cellulose, to render it resistant to wrinkling and creasing which includes the steps of impregnating the textile with an aqueous solution con-

taining the ingredients (1) formaldehyde, (2) the reaction product of tetrahydro-5-ethyl-S-triazone and formaldehyde, and (3) the reaction product of formaldehyde and acetic hydrazide in a molar ratio of formaldehyde to the hydrazide of about 3:1 to 10:1; the total amount of said ingredients in the solution being at least about 5 weight percent and the proportions of said ingredients being about 1 to 20 moles of formaldehyde, about 0.5 to 8 moles of the formaldehyde-triazone reaction product and about 1 mole of the formaldehyde-hydrazide reaction product; and heating the impregnated textile to dry it and provide a textile resistant to creasing and wrinkling.

14. The method of claim 13 in which the aqueous solution also contains a catalytic mixture comprising a mixture of magnesium chloride and maleic acid.

15. A method for the impregnation of a textile, fabricated from a material selected from the group consisting of cellulose and regenerated cellulose, to render it resistant to wrinkling and creasing which includes the steps of impregnating the textile with an aqueous solution containing the ingredients (1) formaldehyde, (2) the reaction product of tetrahydro-5-beta-hydroxyethyl-S-triazone and formaldehyde, and (3) the reaction product of formaldehyde and diglycolic dihydrazide in a molar ratio of formaldehyde to the dihydrazide of about 6:1 to 20:1; the total amount of said ingredients in the solution being at least about 5 weight percent and the proportions of said ingredients being about 1 to 20 moles of formaldehyde, about 0.5 to 8 moles of the formaldehyde-triazone reaction product and about 1 mole of the formaldehyde-hydrazide reaction product; and heating the impregnated textile to dry it and provide a textile resistant to creasing and wrinkling.

16. The method of claim 15 in which the aqueous solution also contains a catalytic mixture comprising a mixture of magnesium chloride and citric acid.

17. A textile, fabricated from a material selected from the group consisting of cellulose and regenerated cellulose, which has been rendered resistant to creasing and wrinkling by the method of claim 7.

18. A cotton textile which has been rendered resistant to creasing and wrinkling by the method of claim 7.

19. A linen textile which has been rendered resistant to creasing and wrinkling by the method of claim 7.

20. A regenerated cellulose rayon textile which has been rendered resistant to creasing and wrinkling by the method of claim 7.

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