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EUROPEAN PATENT APPLICATION

⑳ Application number: **80301460.4**

⑤① Int. Cl.³: **D 06 M 15/66, C 08 L 83/04,**
D 06 M 13/12

㉔ Date of filing: **02.05.80**

③① Priority: **04.05.79 US 36035**
07.05.79 US 36641

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④③ Date of publication of application: **10.12.80**
Bulletin 80/25

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⑧④ Designated Contracting States: **AT BE CH DE FR GB IT**
LI LU NL SE

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⑤④ **A non-formaldehyde durable press textile treatment process, a finishing agent for use in the process and a textile fabric treated by the process.**

⑤⑦ This invention relates to a durable press treatment for textile fabrics containing cellulosic fibers and which is characterized by avoiding the use of formaldehyde and problems associated therewith. The fabric is impregnated with a formaldehyde-free finishing agent containing glyoxal, reactive silicone and a catalyst. The fabric is thereafter dried and the finishing agent is cured to impart durable press properties to the fabric.

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A NON-FORMALDEHYDE DURABLE PRESS TEXTILE
TREATMENT PROCESS, A FINISHING AGENT FOR USE
IN THE PROCESS AND A TEXTILE FABRIC TREATED
BY THE PROCESS

Field of the Invention

This invention relates to a non-formaldehyde durable press finish for textile fabrics and to a novel and advantageous process for imparting durable press properties to a textile fabric characterized by avoiding
5 the use of formaldehyde or formaldehyde-based compounds. The present invention also relates to durable press textile fabrics treated with said non-formaldehyde finish.

Background of the Invention

Formaldehyde has been used in the textile industry for a number of years in a variety of applications.
10 Perhaps one of its widest uses is as an ingredient in durable press finishes for fabrics containing cellulosic fibers. Recently, however, there has been increasing concern over safety and health hazards presented by the
15 use of formaldehyde. It has been determined that exposure to formaldehyde on fabrics or in the air can cause allergic reactions in some persons. It has even been suggested that formaldehyde may be a carcinogenic or mutagenic agent.

20 Because of this concern, efforts are being made in the United States, as well as in other countries, to reduce or eliminate formaldehyde usage wherever possible, including textile uses. In the United States, the amount of formaldehyde which can be discharged into waste water
25 streams is limited by governmental regulation, as is the amount of exposure which workers may have to formaldehyde vapors in the air. In Japan, concern over the safety of

formaldehyde has led to strict regulations prohibiting any free formaldehyde in apparel for children under two years of age and setting limits on the amount of formaldehyde which may be present in adult apparel. It is anticipated that in the near future, other countries may also enact restrictions or prohibitions on the use of formaldehyde in textile finishing.

Presently, all of the commercial durable press treatments for textile fabrics require formaldehyde or formaldehyde-based compounds. Typically, durable press treatments use methylol derivatives of cyclic ureas or methylol carbamates, of which the following are examples: dimethylol ethylene urea (DMEU), ethyl carbamate, and dimethylol dihydroxyethylene urea (DMDHEU). DMDHEU, sometimes called glyoxal resin, is perhaps the most commonly used durable press finishing agent and is formed by reacting urea, formaldehyde and glyoxal. The methylol group ($-\text{CH}_2-\text{OH}$) of all of these durable press agents is formed by formaldehyde and is the group that cross-links with cellulose to give durable press properties. There is no way to prevent some formaldehyde from being released when this cross-linking (curing) occurs. In addition, some free formaldehyde usually remains in the cured fabric. If the residual free formaldehyde is to be removed from the fabric, an afterwashing operation is required, but even this is not totally effective.

Intensive efforts are being made both in the United States and abroad to develop a durable press treatment which eliminates formaldehyde or formaldehyde-based compounds and at least one non-formaldehyde durable press treatment has recently been proposed. Recent U. S. Patent 4,116,625 discloses a non-formaldehyde durable press finish based on imidazoline derivatives combined with acrylic or methacrylic glycidyl containing polymers. It is reported, however, that this process is more expensive and less effective than processes based on formaldehyde, and requires powerful acid catalysts which are of questionable safety.

Therefore, at the present time no commercially acceptable alternatives to formaldehyde-based durable press finishes have been introduced, and formaldehyde is regarded as a "necessary evil" in durable press finishes.

5 The primary approach to the formaldehyde problem has thus been to attempt to reduce formaldehyde levels. Various approaches have been employed, such as varying the catalyst systems used or reducing the amount of formaldehyde-based resin in the finish by employing a
10 resin extender, such as silicone. These approaches are not very effective, however, and the formaldehyde levels in the finishing plant and in the fabric remain undesirably high.

Summary of the Invention

15 The present invention provides a durable press treatment which has succeeded in eliminating any dependence on the use of formaldehyde or formaldehyde-generating chemicals, and thus avoids the attendant problems and hazards of formaldehyde in the finishing
20 operation and in the finished fabric. The present invention achieves durable press fabric properties which are comparable, if not superior, to those obtained by conventional formaldehyde-based durable press treatments. The treatment method can be carried out at a competitive
25 cost and on the same apparatus which is used for conventional formaldehyde-based durable press treatments.

The formaldehyde-free durable press finishing agent of the present invention contains as fiber treating agents a mixture of two readily available materials,
30 glyoxal and reactive silicone. Each of these materials has been previously used in textile finishing applications. However, so far as applicant is aware these two materials have never been used in combination with one another in a process for imparting durable press properties to a
35 fabric.

Reactive silicone, for example, is commercially sold as a softener and resin extender for use in combination with formaldehyde-based durable press resins to

reduce the amount of resin required while also imparting desirable hand properties to the finished fabric. The silicone is thus used as an additive to a resin which itself has the capability of imparting durable press properties to the fabric. By way of example, the effect of silicone on resin treated cellulosic fabrics is considered by Simpson in Textile Research Journal, February 1958.

Glyoxal, as noted earlier, has previously been used as an ingredient in a formaldehyde-based durable press resin. Additionally, several early patents disclose the use of glyoxal for dimensionally stabilizing or shrink-proofing fabrics made of regenerated cellulose, as for example the Pfeiffer, Jr., et al U. S. Patents Nos. 2,412,832; 2,436,076 and 2,530,175.

It is recognized by those knowledgeable in the field of textile finishing that although glyoxal has utility in some applications for shrink-proofing, it is ineffective in imparting durable press properties to a fabric. Additionally, it is also known that the use of glyoxal has undesirable side effects and results in severe loss of fabric strength.

It has been discovered in accordance with the present invention that although reactive silicone and glyoxal are each ineffective by themselves as a durable press agent, their combined use as fiber treating agents imparts effective durable press properties to a fabric and, most significantly, for the first time makes it possible and practical to provide durable press properties in a fabric without the use of formaldehyde or formaldehyde-generating chemicals.

Description of the Drawing

The drawing is a graph comparing the amount of free formaldehyde present in fabrics treated with two conventional formaldehyde-based durable press resins and with the non-formaldehyde durable press finishing agent of the present invention. Free formaldehyde (in parts per million) is plotted against curing time in seconds.

The amount of free formaldehyde in the fabric was determined by the Sealed Jar Method (AATCC Test Method 112-1978). This test method is intended to detect free formaldehyde over a range from about 300 ppm, which is undetectable by the nose, to about 3500 ppm, which is very odoriferous.

The curve indicated by triangles, which shows the highest amount of free formaldehyde, is a commercially available resin which is a blend of urea formaldehyde, DMDHEU, and butyl triazone. The curve indicated by squares is a commercially available DMDHEU (glyoxal formaldehyde-based resin) product. The curve indicated by circles is the non-formaldehyde durable press finishing agent of the present invention. As seen in the graph, the small level of free formaldehyde measured in the non-formaldehyde samples is well below the minimum sensitivity of the current standard test method for formaldehyde detection. Work directed toward a more accurate test method for determination of very small amounts of formaldehyde in a fabric is continuing.

Durable press fabrics produced in accordance with the present invention are thus essentially free of formaldehyde. Any formaldehyde which might be found in the fabric would be attributable either to impurities present in the glyoxal or other reactants, degradation of the glyoxal, or pick-up from formaldehyde vapors present in the air. There is no purposeful addition of formaldehyde to the finish formulation.

Detailed Description of the Invention

The non-formaldehyde durable press treatment of the present invention is applicable to textile fabrics which are formed at least partially of cellulosic fibers, such as cotton and synthetic fiber blend fabrics as well as 100% cotton fabrics.

The finishing agent may be applied to the fabric in the same manner that conventional formaldehyde-based durable press finishes are applied, such as for example

by impregnation with an aqueous bath or foam of the finishing agent. The fabric is then dried and thereafter cured by heating.

The invention is applicable for producing both precured and postcure fabrics. As is well known, precured
5 fabrics are cured during the finishing operation, usually immediately following drying of the impregnated fabric. In postcure fabrics, the fabric is impregnated with the finishing agent and dried, but the curing is performed at a later time, usually after the fabric has been cut and
10 formed into garments.

In a preferred method of application, the fabric is impregnated by padding with an aqueous bath of the non-formaldehyde finishing agent to obtain a wet pick-up of about 45 to about 100 percent by weight. The fabric is
15 then dried on a tenter frame operating at an elevated temperature of up to about 300° F. If the fabric is to be postcured, it is dried to a moisture content of about five to ten percent and then removed from the tenter frame. If the fabric is to be precured, curing may be carried out on
20 the tenter frame immediately following drying by heating the fabric in a curing chamber at a temperature of about 350 - 400° F for up to about two minutes until sufficiently cured. Following curing, the fabric may be subjected to an after-washing operation if desired.

25 Glyoxal for use in the present invention is available in commercial quantities as an aqueous solution, usually about 40 percent concentration.

The reactive silicone materials which may be suitably employed in the present invention are available
30 from various manufacturers. These materials are designed and sold for use as softening agents and durable press resin extenders for textile finishing applications. They generally are available as stable reactive organosilicone emulsions which are readily dilutable with water. Manu-
35 facturers sometimes recommend that the reactive silicone material be used in conjunction with cross-linking additives, such as silane, but when employed pursuant to the

present invention, the cross-linking additive is not essential. Suitable results have been observed both with and without use of the recommended cross-linking additives. Illustrative, but non-limiting examples of suitable reactive silicones include General Electric Silicone Softener/
5 Resin Extender SM2129, Dow Corning 1111 Silicone Emulsion, Union Carbide Y-9224 Silicone Emulsion and General Electric Silicone Softener/Resin Extender XM-124-5557.

The glyoxal and reactive silicone fiber treating
10 agents are applied to the fabric in the presence of a catalyst. Catalysts suitable for use with conventional formaldehyde-based durable press resins may also be used with the non-formaldehyde finishing agent of the present invention. Conventional durable press catalysts include
15 metal salt catalysts, latent catalysts, and acid or acid salt catalysts. Illustrative, but non-limiting examples of such catalysts include the following: zinc fluoborate, ammonium chloride, magnesium chloride, ammonium phosphate, ammonium sulfate, amine hydrochlorides, and zinc nitrate.

20 A number of the conventional durable press catalysts, when used with the non-formaldehyde durable press finishing agent of the present invention, have been found to cause discoloration or change of shade in the fabric when allowed to remain on the fabric following
25 curing. However, these catalysts may be suitably used with the present invention with no adverse effect when the fabric is subjected to an after-washing operation following curing, since the catalysts are removed from the fabric by the after-washing treatment.

30 It has been found, however, that the undesirable after effects produced by some of the conventional durable press catalysts may be avoided by using as a catalyst in the present invention a metal sulfate salt. Particularly suitable as a catalyst is a metal sulfate blend which
35 comprises a mixture of aluminum sulfate and magnesium sulfate in substantially equal proportions.

In accordance with a further aspect of the present invention there may be incorporated in the non-formaldehyde durable press finish formulation an additional agent for reducing the acidity of the finished fabric. This additional agent is referred to herein as a buffering agent since it is believed to form a buffer system in the aqueous finish formulation which results in moderating the strongly acid characteristics of the glyoxal in the finished fabric. However, regardless of the actual theory or chemical mechanism by which the agent operates, the function of the agent is to decrease the acidity of the finished fabric, and it is highly important that this be accomplished without counteracting the ability of the glyoxal and reactive silicone fiber treating agents for imparting durable press properties to the fabric.

Illustrative but non-limiting examples of compounds which have been found suitable as agents for decreasing the acidity of the finished fabric include sodium hydrogen phosphate, sodium dihydrogen phosphate, potassium carbonate, sodium carbonate, potassium citrate, sodium citrate, sodium oxalate, sodium acetate, sodium tartrate, borax, sodium metaborate, and mixtures of two or more of these salts. A preferred class of such agents are the alkali metal salts of weak acids.

These compounds are used in relatively small amounts in the non-formaldehyde finish formulation. The amount of the compound used depends upon the characteristics of the particular compound, the amount of glyoxal in the finish formulation and the final fabric pH desired. Preferably, it is used in an amount sufficient to achieve

a pH of at least 4, and preferably 4.5 in the finished fabric. Typically, this represents about 20 to 60% by weight buffering agent, based on the solids content of the glyoxal.

5 It has been observed that certain salts which are useful as buffering agents may reduce the effectiveness of the fiber treating agents in providing durable press properties, and for this reason, the buffering agent is preferably used in the smallest amount possible which
10 provides adequate reduction in acidity.

 It is also believed that certain of the buffering agents may also in some way interact with the catalyst, lessening its effectiveness and thus resulting in a reduction in durable press performance. Additionally,
15 certain of the buffering agents have in some instances been observed to cause discoloration or change of shade in the fabric.

 After extensive investigation of numerous possible buffering agents and combinations thereof, it has
20 been determined in accordance with the present invention that sodium metaborate octahydrate is a highly effective agent for reducing the fabric acidity and the preferred agent for use in the non-formaldehyde durable press formulation of the present invention. This compound also
25 avoids undesirable side effects such as fabric discoloration or change of shade. Additionally, when this compound is used in combination with the preferred metal sulfate blend catalyst described above, very little interference or interaction with the catalyst is observed.

30 The formaldehyde-free finishing agent of the present invention may optionally include small amounts of a wetting agent for facilitating the wetting and penetration of the finishing agent into the fabric. Particularly suitable as wetting agents are nonionic surfactants such
35 as ethoxylated decyl alcohols, ethoxylated nonyl alcohols, ethoxylated secondary alcohols, and alkylaryl polyether

alcohols. Illustrative but non-limiting examples of suitable commercially available wetting agents are: Triton X-100, a product of Rohm and Haas, and MYKON NRW, available from Sun Chemical Corporation.

5 Other conventional textile finishing modifiers or additives may be incorporated in the formulation, if desired, including hand builders or hand modifiers such as polyvinyl acetate or acrylic resins, softeners, soil release agents, etc.

10 The glyoxal and reactive silicone fiber treating agents have been found to be effective in providing durable press properties at very low concentration levels on the fabric. In some instances, for example, . acceptable durable press properties have been achieved
15 with as little as one-third of one percent glyoxal or as little as one-fourth of one percent reactive silicone, by weight based on the dry weight of the fabric. However, concentrations somewhat higher than this are usually preferred in order to obtain consistently good results.
20 The upper limit on the amount of glyoxal and silicone is primarily a practical limit dictated by economics. Fabric properties and durable press performance are not significantly improved by increasing the concentration levels of the fiber treating agents above the preferred
25 levels, but no adverse effects on durable press properties are observed.

 The preferred concentration levels of the fiber treating agents vary depending upon the fiber content, the weight and construction of the fabric, and on other
30 factors. Fiber blend fabrics, such as cotton and polyester fiber blends, for example, will require a lower concentration level of fiber treating agents than fabrics formed wholly of cotton fibers to achieve comparable durable press properties.

35 For the range of fiber contents, fabric styles, weights, and constructions which are normally encountered, it has been found desirable to apply to the fabric a

glyoxal concentration within the range of about one to about eight percent and a reactive silicone concentration within the range of about one-third of one percent to about one percent, by weight based on the dry weight of the fabric.

For synthetic fiber and cotton blend fabrics containing up to about fifty percent cotton fibers, a concentration range of about one and one-half percent to about three percent glyoxal and about one-third percent to about two-thirds percent reactive silicone is preferred. For fabrics formed wholly or predominantly of cotton fibers, a higher glyoxal concentration of about three percent to about seven percent is preferred, with the silicone concentration preferably remaining within the range of about one-third percent to about two-thirds percent, by weight based on the dry weight of the fabric.

In the aqueous finishing bath the concentration of the fiber treating agents, catalyst and other ingredients in the aqueous finishing bath may vary depending upon a number of factors, such as the method of application, wet pick-up achieved, desired concentration on fabric, etc. Preferably, however, these materials are present in proportions by weight generally as follows:

glyoxal (solids basis)	100 parts
25 catalyst (active solids basis)	5-40 parts
reactive silicone (solids basis)	3-75 parts
buffering agent (solids basis)	0-60 parts
wetting agent (wet basis)	up to about 15 parts
other additives, modifiers,	
30 etc. (solids basis)	up to about 200 parts

A particularly preferred formulation is as follows:

glyoxal (solids basis)	100 parts
metal sulfate blend catalyst	
35 (active solids basis)	12 to 23 parts
reactive silicone (solids basis)	18 to 43 parts
sodium metaborate octahydrate	
buffering agent (solids basis)	30 to 40 parts
wetting agent (wet basis)	up to about 15 parts
40 other additives, modifiers, etc.	
(solids basis)	up to about 200 parts

The invention is further illustrated by the following examples in which all parts and percentages are by weight unless otherwise indicated. These non-limiting examples are illustrative of certain embodiments of the invention and are designed to teach those skilled in the art how to practice the invention and the best mode contemplated for carrying out the invention.

EXAMPLE 1

A non-formaldehyde durable press finish bath was formulated by diluting about 110 lbs. of commercial glyoxal (40 percent aqueous solution) with about 50 gallons of water, and to this diluted solution adding three pounds of an ethoxylated decyl alcohol nonionic surfactant (MYKON NRW), 27.5 pounds of metal sulfate blend catalyst (a 50/50 mixture of aluminum sulfate and magnesium sulfate at a 30 percent concentration), 46 pounds of reactive silicone (General Electric Silicone Softener/Resin Extender XM-124-5557) containing 25 percent by weight active solids, and 20 pounds of polyvinyl acetate hand builder (SEYCO REZ B-47 produced by AZS Chemical Company of Atlanta, Georgia). Water was then added to make a total of 150 gallons of mix. This finishing bath formulation was piped to a three-roll padder and a 65/35 polyester/cotton blend twill weave fabric weighing about 7.3 ounces per square yard was directed through the padder where it was immersed in the finishing bath and squeezed to remove excessive finish and to provide a wet pick-up of about 55 percent. After the finishing bath formulation was applied, the fabric was dried on a tenter frame operating at a temperature of about 250 - 300° F, and then directed through a curing oven at a temperature of about 375 - 400° F for about one minute to cure the finishing agent.

The impregnation of the fabric with the finishing bath provided a weight percent concentration of solids on the dried fabric calculated to be as follows:

wetting agent	.034%
glyoxal	1.84 %
metal sulfate blend catalyst	.34 %
reactive silicone	.48 %
5 polyvinyl acetate	.46 %

The amount of formaldehyde was checked at the exhaust of the tenter frame during the run, but no formaldehyde was detected. The finished fabric was also tested and a free formaldehyde content of 150 ppm was measured, 10 which as noted earlier is below the minimum sensitivity of the test method.

Physical properties of the fabric were measured using standard AATCC test methods. Durable press properties were determined by rating the fabric smoothness 15 appearance after five home washings on a scale of 1 to 5 with reference to standard fabric smoothness test specimens (AATCC Test Method 124-1978). The following results were observed:

20	breaking strength, lbs. W.	236
	" " F.	127
	tearing strength, gms. W.	6400
	" " F.	5450
	finished weight, oz./sq. yd.	7.5
	construction W.	86
25	" F.	48
	fabric appearance	4
	fastness to: washing - stain	3-4
	washing - color chg.	4
	chl. blch. - stain	3-4
30	chl. blch. - color chg.	3-4
	light	4
	pH of fabric	3.6
	ppm formaldehyde	150

The fabric physical properties were fully satisfactory. 35 The fabric smoothness appearance rating of 4 represents acceptable durable press performance.

EXAMPLE 2

A 5.3 ounce twill weave shirting fabric containing 65 percent polyester fibers and 35 percent cotton 40 fibers was directed through a padder and impregnated with the following formulation:

glyoxal (40%) 95 lbs.
 sulfate blend catalyst (50% aluminum sulfate/50% magnesium sulfate) 25 lbs.
 anionic surfactant (HIT Wet WR) 3 lbs.
 5 G. E. Silicone XM-124-5557 46 lbs.
 polyvinyl acetate 22.5 lbs.
 acetic acid 2 lbs.
 water to make 150 gallons

The fabric was squeezed to a 50 percent wet pick-up, there-
 10 after dried on a tenter frame, and then directed through a
 curing oven at a temperature of 375 to 400° F for about one
 minute. Fabric physical properties and appearance were
 measured using standard AATCC test methods and the test
 results are shown in Table 1.

15 For comparison, the same fabric was treated
 under similar conditions with a conventional DMDHEU durable
 press resin, and the test results are also shown in Table
 1.

Table 1

20		Non-Formaldehyde	DMDHEU
		Finish	Control
	breaking strength, lbs. W.	188	192
	" " " F.	72	75
	tearing strength, gms. W.	5800	4000
25	" " " F.	3800	2650
	finished weight, ozs./sq. yd.	5.3	5.3
	construction W.	125	128
	" F.	49	50
	fabric appearance	4	4
30	fastness to: washing - stain	3	3
	color change	4	4
	chl. blch. - stain	3	3
	chl. blch. - col. chg.	4	4
	light	4	4
35	ppm formaldehyde	75	300
	pH of fabric	5.0	--

The cost of the non-formaldehyde finish was com-
 parable to the DMDHEU resin. The physical properties were
 comparable to or better than the DMDHEU control, and the
 40 fabric smoothness appearance ratings were the same. This
 test showed the non-formaldehyde durable press finish to
 be an acceptable alternative to the formaldehyde-based
 DMDHEU resin.

EXAMPLES 3 to 6

Samples of a 7.2 ounce/square yard fabric (65 percent polyester/35 percent cotton) were impregnated with various finish formulations, and were dried and cured under similar conditions. Comparisons of the durable press properties were made by rating the fabric appearance after five home washings (AATCC Test Method 124-1978 and/or by measuring the crease recovery angle in the warp and filling direction (Monsanto test).

10 EXAMPLE 3 - GLYOXAL PLUS REACTIVE SILICONE

Tests were made varying the type and amount of reactive silicone in the finish, with the following results:

		<u>% solids applied (by weight)</u>		
15	wetting agent	.034	.034	.034
	glyoxal	1.59	1.59	1.59
	sulfate blend catalyst	.31	.31	.31
	G. E. Silicone XM-124-5557	.48	--	--
	Dow Corning 1111 silicone			
20	emulsion	--	.67	.48
	Dow Corning T4-0149 additive	--	--	.14
	polyvinyl acetate	.46	.46	--

		<u>Test Results</u>		
	appearance after 5 HW	4	4	4
25	crease recovery angle, W + F, as received	298	310	310

EXAMPLE 4 - SILICONE VARIATIONS

Tests were made using reactive silicone without glyoxal and using glyoxal with various levels of silicone.

30 The following results were observed:

		<u>% solids applied</u>			
	wetting agent	.034	.034	.034	.034
	glyoxal	----	1.59	1.59	1.59
	sulfate blend catalyst	.31	.31	.31	.31
35	G. E. Silicone XM-124-5557	.48	----	.34	.48
	polyvinyl acetate	.28	.28	.46	.46

		<u>Test Results</u>			
	crease recovery angle, W + F, as received	220	275	307	298
40	While the crease recovery was undesirably low when glyoxal alone or silicone alone was used, a dramatic improvement				

in crease recovery was observed when the two were used in combination. Increasing the amount of silicone from .34 to .48 percent provided no additional improvement in crease recovery for this fabric.

5 EXAMPLE 5 - GLYOXAL VARIATIONS

Runs with various levels of glyoxal ranging from .28 percent to 2.75 percent were made on a 5.1 ounce and 7.2 ounce fabric, with the following exemplary results:

		<u>% solids applied</u>					
10	fabric weight, ozs. (65% polyester/ 35% cotton)	5.1	5.1	7.2	5.1	7.2	7.2
	wetting agent	.034	.034	.034	.034	.034	.034
	glyoxal	.28	.32	.38	2.75	2.75	4.4
15	sulfate blend						
	catalyst	.054	.061	.073	.54	.54	.31
	G.E. Silicone XM- 124-5557	.67	---	---	---	---	.48
20	Dow Corning T4-0149 additive	---	.14	.14	.14	.14	---
	Dow Corning 1111 emulsion	---	.48	.48	.48	.48	---
	polyvinyl acetate	.42	.42	.42	.48	.48	.51

		<u>Test Results</u>					
25	appearance after 5 HW	3.5	3	4	4	4	4
	crease recovery angle						
	W+F, as received	271	302	273	319	309	290

Good results were observed with as low as 0.32 percent glyoxal on the 5.1 ounce fabric, but higher levels of glyoxal were required before consistently good results were observed. Increasing the glyoxal concentration from 2.75 percent to 4.4 percent showed no additional improvement in appearance or crease recovery. The upper limitation on the amount of glyoxal which may be used thus appears to be merely an economic limitation.

EXAMPLE 6 - CATALYSTS

On 7.2 ounce fabric (65 percent polyester/35 percent cotton):

		<u>% solids applied</u>				
5	wetting agent	.034	.034	.034	.034	.034
	glyoxal	1.88	1.88	1.59	1.59	1.59
	sulfate blend catalyst	.37	--	.31	.22	.15
	magnesium dihydrogen phosphate catalyst	--	.34	--	--	--
10	G. E. Silicone XM-124-5557	.48	.48	.48	.48	.48
	polyvinyl acetate	.49	--	.46		

		<u>Test Results</u>				
	appearance after 5 HW	4	4	4	4	4
15	crease recovery angle, W + F, as received	293	310	298	338.	303

Good fabric appearance and crease angle were observed with both the sulfate blend catalyst and the phosphate catalyst, even as low as .15 percent catalyst.

20 However, slight fabric discoloration was observed with the phosphate catalyst.

EXAMPLE 7 - POSTCURE

Examples 3 to 6 above were precured, i.e. the fabric was fully cured at 350 - 400° F after drying. The example below was postcured, meaning that the fabric was dried only to about 5 percent moisture content and then later cured at 325 - 350° F for several minutes. Cutters would buy this non-cured fabric and make it into garments before pressing and curing.

		<u>% solids applied</u>
30	wetting agent	.034
	glyoxal	1.59
	sulfate catalyst	.31
	G. E. Silicone XM-124-5557	.48
35	polyvinyl acetate	.46

		<u>Test Results</u>
	appearance after 5 HW	4
	crease recovery angle, W + F, after curing	290
40	crease appearance after 5 HW	5

EXAMPLE 8

Samples of a 9 ounce/square yard twill weave fabric containing 50 percent polyester fibers and 50 percent cotton fibers were impregnated with various finish formulations and were dried and cured under similar conditions. Comparisons of the durable press properties were made by rating the fabric appearance after five home washings (AATCC Test Method 124-178) and by measuring the crease angle in the warp and filling direction (Monsanto test). The following results were observed:

	<u>% solids applied</u>					
wetting agent	.034	.034	.034	.034	.034	.034
glyoxal	1.84	2.30	2.76	3.22	3.68	4.15
sulfate catalyst	.31	.31	.31	.31	.31	.31
silicone	.48	.48	.48	.48	.48	.48
polyvinyl acetate	.46	.46	.46	.46	.46	.46

	<u>Test Results</u>					
appearance after 5 HW	4	4	4	4+	4	4
crease recovery angle W+F, as received	281	289	294	301	285	296

Acceptable durable press qualities were observed as low as 1.84 percent glyoxal. Performance improved slightly as the glyoxal concentration was increased to 2.30, but further increases did not produce significant improvement.

EXAMPLE 9

Samples of a 10 ounce/square yard twill weave fabric (100 percent cotton) were impregnated with various finish formulations and were dried, cured, and tested as in Example 8. The following results were observed:

	<u>% solids applied</u>		
wetting agent	.034	.034	.034
glyoxal	3.68	4.61	6.45
sulfate catalyst	.31	.31	.31
silicone	.48	.48	.48
polyvinyl acetate	.46	.46	.46

Test Results

	appearance after 5			
	HW	4-	3+	4
	crease recovery angle,			
5	W+F, as received	281	288	294

The sample containing 6.45 percent glyoxal exhibited fully acceptable durable press properties.

EXAMPLE 10

To a 40 percent aqueous glyoxal solution, sodium hydroxide (25 percent aqueous solution) was added dropwise while stirring until the glyoxal was brought from an initial pH of about 2.6 to a substantially neutral pH of about 7. To this solution was added magnesium dihydroxide phosphate catalyst, polyvinyl acetate, a wetting agent, reactive silicone, and water, to produce a finishing bath formulation of the composition shown below. This formulation was applied to a 65/35 polyester/cotton blend fabric at a 55 percent pick-up and the fabric was dried and cured to a concentration on the fabric as shown below (percent active solids by weight):

	<u>in bath</u>	<u>on fabric</u>
wetting agent	.06	.03
glyoxal	3.4	1.9
phosphate catalyst	.6	.34
25 reactive silicone	.88	.48
polyvinyl acetate	1.67	.92

The sample was tested for fabric appearance, crease angle and pH with the following results:

	crease recovery angle	286
30	fabric appearance	4
	fabric pH	4.6

EXAMPLE 11

10 A non-formaldehyde durable press finish formulation was prepared as follows:

15 15.4 lbs. of sodium metaborate oxyhydrate was added directly to about 110.4 lbs. of commercial glyoxal (40 percent aqueous solution) and was stirred and dissolved. The resulting solution contained about 12.4 percent by weight sodium metaborate oxyhydrate. This solution was diluted with about 50 gallons of water, and to the diluted solution was added three lbs. of an ethoxylated decyl alcohol nonionic surfactant (MYKON NRW), 27.5 lbs. of metal sulfate blend catalyst (50/50 mixture of 20 aluminum sulfate and magnesium sulfate at a 30 percent concentration), 46 lbs. of reactive silicone (General Electric Silicone Softener/Resin Extender XM-124-5557) containing 25 percent by weight active solids, and 20 lbs. of polyvinyl acetate hand builder (SEYCO REZ B-47, 25 produced by AZS Chemical Company of Atlanta, Georgia). Water was then added to make a total of 150 gallons of mix.

30 This finishing bath formulation was piped to a three roll padder and a 65/35 polyester/cotton blend twill weave fabric weighing 7.3 ounces per square yard was directed through the padder where it was immersed in the finishing bath and squeezed to remove excessive finish and provide a wet pick-up of about 61.5 percent. After the finishing bath formulation was applied, the 35 fabric was dried on a tenter frame operating at a temperature of about 250 - 300° F.

The percent solids deposited on the fabric was calculated to be as follows (percent by weight, based on the dry weight of the fabric):

	glyoxal	2.17%
5	sodium metaborate (hydrated)	0.24%
	metal sulfate blend catalyst	0.34%
	reactive silicone	0.57%

A portion of this fabric was precured while on the tenter frame by directing the same immediately from the drying zone through a curing oven at a temperature of 350 - 400° F for about one minute. Another portion of the fabric was removed from the tenter frame after drying and postcured at a later time by heating at a temperature of about 350° F for about one minute. Physical properties and durable press performance of both the precured and the postcured fabric were measured using standard AATCC test methods, with the following results:

<u>Test</u>		<u>Precured</u>	<u>Postcured</u>
	breaking strength, lbs. W.	219	214
20	" " " F.	99	96
	tearing strength, gms. W.	6400	6400
	" " " F.	5000	5150
	finished weight, oz./sq. yd.	7.1	7.3
	construction W.	86	86
25	" F.	42	43
	fabric appearance	4	4
	crease appearance	--	5
	fastness to: washing - stain	3-4	3-4
	washing - color chg.	4	4
30	chl. blch. - stain	3-4	3-4
	chl. blch. - color chg.	3	3
	light	3-4	3-4
	pH of fabric	5.1	5.1
	ppm formaldehyde	120	125

The physical properties of both the precured and the postcured fabrics were fully satisfactory. The fabric smoothness appearance rating of 4 and the crease appearance of 5 represent acceptable durable press performance. The level of free formaldehyde measured in the fabric samples is below the minimum sensitivity of the test method.

The fabric pH of 5.1 was acceptable without the need for an after-wash operation. By comparison, the same finish formulation with the sodium metaborate omitted produced a finished fabric pH of about 3.5, which would ordinarily require afterwashing to reduce fabric acidity.

EXAMPLES 12 - 16

Samples of a 7.2 ounce/square yard twill weave 65/35 polyester/cotton blend fabric and a 9 ounce/square yard twill weave 50/50 polyester/cotton blend fabric were impregnated with various finish formulations, and were dried and cured under similar conditions. Comparisons of the durable press properties were made by rating the fabric appearance after five home washings (AATCC Test Method 124-1978) and fabric pH was measured. The percent solids deposited on the fabric was calculated for each fabric sample, based upon the finishing bath composition and the percent pick-up. The percent solids on fabric (percent by weight based on the dry weight of the fabric) and the corresponding fabric appearance and fabric pH for each sample were as follows:

<u>EXAMPLE</u>	12	13	14	15	16
fabric (% polyester/ % cotton)	65/35	65/35	65/35	50/50	50/50
wetting agent	.028	.034	.034	.028	.028
glyoxal	2.64	1.94	1.94	4.4	3.3
sodium metaborate octahydrate	.94	.69	.96	2.62	1.17
metal sulfate blend catalyst	.45	.36	.36	.8	.56
reactive silicone	.48	.5	.5	.48	.48
polyvinyl alcohol	.46	.48	.48	--	.46
appearance	4	4	4	4	4
fabric pH	4.6	4.9	4.9	4.5	4.35

From the foregoing description and examples it will thus be seen that the present invention has provided a practical and effective improved durable press finish formulation and treatment method which has succeeded in

eliminating any dependence on the use of formaldehyde or formaldehyde-generating chemicals, and thus avoids the attendant problems and hazards of formaldehyde in the finishing operation and in the finished fabric.

5 While the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications may be made within the spirit and scope of the invention as described above and as defined in the
10 appended claims.

CLAIMS

1. A process for imparting durable press properties to a textile fabric formed at least partially of cellulosic fibers and which avoids the use
5 of formaldehyde and problems associated therewith, characterized by impregnating the textile fabric with a formaldehyde-free finishing agent comprising glyoxal, reactive silicone and a catalyst, and thereafter drying the fabric and curing the finishing agent to impart
10 durable press properties to the fabric.

2. A process according to Claim 1 wherein the formaldehyde-free finishing agent contains about 3 to 75 parts by weight reactive silicone solids per 100 parts by weight glyoxal solids.

3. A process according to Claim 1/^{or 2} wherein the impregnating of the fabric is carried out so as to provide a pick-up of about 1% to about 8% glyoxal and about 1/3% to about 1% silicone, by weight, based on the dry weight
5 of the fabric.

4. A process according to Claim 1/^{2 or 3} wherein said finishing agent additionally comprises a buffering agent for reducing acidity in the treated fabric.

5. A process according to Claim 4 wherein said buffering agent comprises sodium metaborate.

6. A process for imparting durable press properties to a textile fabric formed at least partially of cellulosic fibers and which avoids the use of formaldehyde and problems associated therewith,

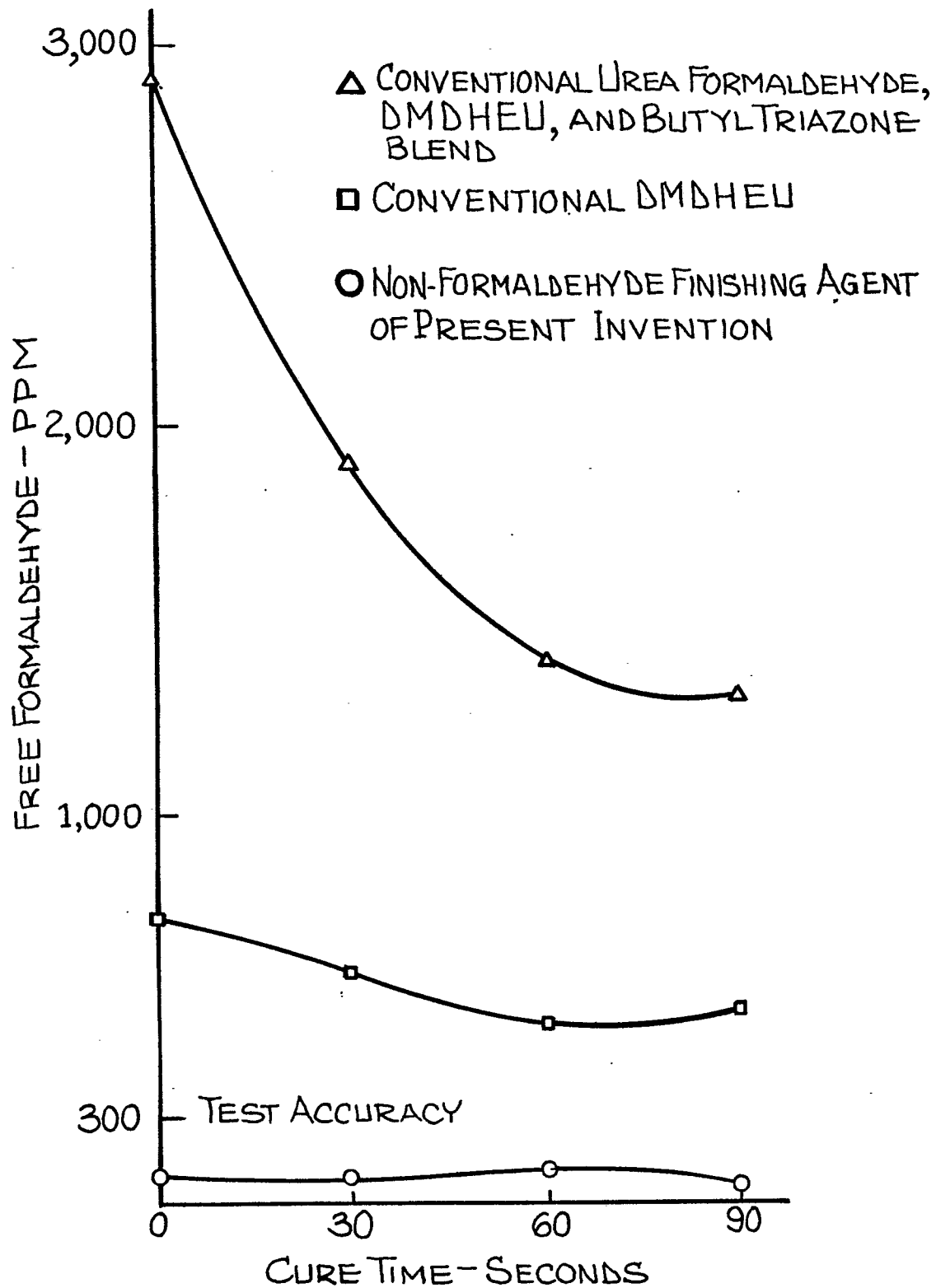
5 characterized by impregnating the fabric with a formalde-
hyde-free finishing agent which contains as fiber treating
agents a mixture of glyoxal and reactive silicone and
which also contains a durable press catalyst, and obtaining
on the fabric a glyoxal concentration within the range of
10 about 1% to about 8% and a reactive silicone concentration
within the range of about 1/3% to about 1% by weight based
on the dry weight of the fabric, drying the impregnated
fabric, and heating the fabric to effect curing of the
finishing agent and to impart durable press properties
15 to the fabric.

7. A durable press textile fabric produced in
accordance with the process set forth in any one of Claims
1 to 6.

8. A non-formaldehyde finishing agent for
imparting durable press properties to a textile fabric
formed at least partially of cellulosic fibers, said
agent being characterized by a formaldehyde-free aqueous
5 composition containing glyoxal, reactive silicone, and a
durable press catalyst.

9. A treated textile fabric formed at least
partially of cellulosic fibers and adapted for being
cured by heating to impart durable press properties to
the fabric but without the use of formaldehyde and
5 problems associated therewith, said textile fabric con-
taining an uncured formaldehyde-free finishing agent as
set forth in Claim 8.

10. A textile fabric according to Claim 9 containing from about 1 to about 8% glyoxal and from about 1/3% to 1% reactive silicone, by weight based on the dry weight of the fabric.





European Patent
Office

EUROPEAN SEARCH REPORT

0020034
Application number

EP 80 30 1460

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	FR - A - 1 299 236 (WACKER) * Whole document * -- TEXTILBETRIEB, vol. 95, no.12, December 1977, Vogel-Verlag Würzburg, DE H. MARWITZ "Vernetzbare Silikone in der Textilveredlung" pages 80-83. * Page 82, right-hand column, lines 6-13; page 80, right-hand column, paragraph 3 * --	1,8 1,8	D 06 M 15/66 C 08 L 83/04 D 06 M 13/12
A	CHEMICAL ABSTRACTS, vol. 85, 1976, page 84, abstract 161737r, Columbus, Ohio, USA MORI et al. "Decrease in the amount of formaldehyde liberated from resin-treated fabrics and fabrics absorbing formaldehyde vapor by dipping in water or washing, and the absorption of formaldehyde liberated from dress shirts by underwear during wearing" & Sen'i Gakkaishi, 1976, 32(8), T-359-T-363. * Whole abstract * ----	1,8	TECHNICAL FIELDS SEARCHED (Int.Cl. 3) D 06 M 15/66 13/12 C 08 G 77/38 C 08 L 83/06 83/04
			CATEGORY OF CITED DOCUMENTS X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family, corresponding document
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
The Hague	20-08-1980	HELLEMANS	