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METHOD OF STERILIZING HYGIENIC
PAPER WARE

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2 Claims. (Cl. 21—2)

This application is a continuation-in-part of my earlier copending application Ser. No. 242,366 filed Dec. 5, 1962, and now abandoned.

The present invention relates to a method of sterilizing hygienic paper ware, such as bandages, catamenial padding, handkerchiefs, towels, insulating pads, babies napkins, paper waddings, which latter in a textile cover can be used as quilts, and to hygienic paper ware sterilized according to said method.

Hygienic paper articles, of the above types, have long been known and are at present being marketed all over the world in an unsterilized condition. Paper bandages are particularly very attractive, being considerably cheaper than those of cotton or other textile fibers, and because, especially in the form of cellulosic wadding, it has a very high absorption capacity for moisture. Paper material having a high moisture absorbing capacity, however, especially cellulosic wadding, has a very poor wet strength.

The latter drawback also occurs with paper babies' napkins but has been obviated by the addition of one or more layers of paper material having a high wet strength, which is obtained by adding during the wet stage of the manufacturing process, preferably in the beater, a formaldehyde resin to the paper pulp, for example, a urea-formaldehyde resin, a melamine formaldehyde resin, or a phenol formaldehyde resin. The addition of 0.5–4% by weight of such resins to impart a high wet strength to the paper is generally known. The addition of such a resin also reduces formation of dust.

When added in a water soluble form, e.g. as a water soluble precondensate in the wet stage of the paper making process, a relatively small quantity of resin is needed to impart a good wet strength to the paper. This is due to the fact, that under these circumstances the resin tends to firmly adhere the paper fibres to each other. When however the same resin is applied to a finished paper material it is not possible to obtain a paper material suitable to be converted into hygienic paper ware.

Accordingly the use of paper material to which resins have been added after the wet stage of the paper making process in the practice of the present invention is not contemplated.

If such resins in a water soluble form have been added to the paper pulp, preferably in the beater and the pulp is then conducted over the paper making machine, the resin is cured during the heating in the dry part of the paper making machine to form a water insoluble resin. Though on leaving the paper machine the resin has become water insoluble the curing is not complete. During subsequent storage, the curing continues for several weeks and then stops. Generally speaking, the resin is cured more completely when the paper on the paper making machine has been heated at a higher temperature and for a longer time. In all cases however the resins in commercially available paper ware are only partially cured.

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Since soft and absorbent paper ware is heated on the paper machine for a very short time (less than one minute) only, the degree of curing of any resins present in them is relatively low, though sufficient to make the resins water insoluble and to impart wet strength to the paper.

In many cases it is desirable or necessary to sterilize hygienic paper ware, and especially paper bandages, before use.

It is known that, in general, articles can be sterilized by dry-heating, e.g. at 180° C. This temperature, however, is unallowably high for all paper ware, and especially for paper bandages.

It is also known that all sorts of articles can be sterilized by heating with steam at 120–140° C. For absorbent paper ware this is not desirable, since paper material without a resin is apt to deteriorate under these conditions, and paper material which has been given a high wet strength by a formaldehyde resin incorporated in it during the wet stage of the process will lose this strength due to the resin being affected. For this reason, "wet" sterilization methods for paper material which has to retain a high wet strength are excluded.

There is a third known method of sterilizing, namely, heating in the presence of a sterilizing gas, e.g. formaldehyde or ethylene oxide, which is separately supplied for the purpose. The sterilization of finished and packed articles by formaldehyde gas is notoriously unreliable because of the slow penetration of the said gas, whereas sterilization by ethylene oxide is economically disadvantageous.

There is accordingly a need for a simple, cheap and reliable method for dry sterilizing hygienic paper ware, for example, by dry-heating at temperatures up to about 150° C.

It has now been found that such hygienic paper ware into at least part of which a formaldehyde resin has been introduced, by adding it to the paper pulp during the wet stage of the paper making process, can be simply and fully sterilized without impairing the wet strength or the absorbency by dry-heating such paper ware, at 60–150° C. for at least 30 minutes. The term "dry-heating" as used in this application is to be understood as the heating of paper ware whose water-content is not higher than air-dry. Air-dry paper ware may contain up to 12% by weight of water. At temperatures below 60° C. no appreciable quantity of formaldehyde is released from the resin, and heating above 150° C. is detrimental to the paper. Naturally the treatment at lower temperatures should be continued for a longer period than at higher temperatures. Moreover, the period of sterilization depends on the nature of the organisms present and on the degree of sterilization required. In most cases, a sterilization for 1–2 hours at 100–110° C. is sufficient, but also in many cases a period of 30 minutes is satisfactory.

It is believed, that the sterilizing action is due to the release of formaldehyde during the further condensation of the partially cured resin. These partially cured formaldehyde resins do not contain free formaldehyde, but they contain many $-\text{CH}_2\text{OH}$ groups. During further heating these may either be split off as free formaldehyde or they may react with other reactive groups in the resin to provide further curing. The total quantity of formaldehyde released depends on many factors, such as the temperature, the kind of resin starting material and the initial degree of curing. In all cases however there is enough formaldehyde released by prolonged heating, e.g. 30 minutes or more, to effect complete sterilization.

It has been found, that after sterilization according to the invention there usually remain ample $-\text{CH}_2\text{OH}$ groups in the resin to sterilize the paper ware again if it should happen to be contaminated after the first sterilization.

Suitable formaldehyde resins are urea, melamine, and phenol formaldehyde resins or mixtures thereof. Of these, the two first-mentioned resins are the most suitable. All commercial resins, which are marketed for imparting a high wet strength to paper, can be used without any further treatment, and they may be added to the wet paper pulp from which the paper material for the hygienic articles or for the resin-containing part thereof, preferably in the beater. The proportion of resin is mostly 0.5–4% by weight, and in most cases preferably 2% by weight of resin, calculated on the air-dry paper.

Suitable water soluble resins for imparting wet strength are phenol formaldehyde resins having a phenol:formaldehyde ratio of approximately 2:3. For urea formaldehyde resins the corresponding ratios are 1:2 and preferably 1:2.5. For melamine formaldehyde resins the ratio is 1:1 and preferably 2:3. The nitrogen content is then roughly 25%. Obviously in each case the molecular weight of the condensed resin depends on the degree of condensation, which in turn depends on the heating conditions in the paper making machine.

A wide variety of such resins for imparting wet strength are available commercially. All these resins have in common the property that only part of the CH_2OH groups present in the uncured resin react during the partial curing on the paper making machine and during subsequent stages, so that sufficient $-\text{CH}_2\text{OH}$ groups remain available to develop formaldehyde vapour during subsequent heating.

Examples of commercially available resins are:

Trademark	Manufactures	Type
Urecoll K	BASF	Urea Formaldehyde.
Ukadan P 6	Schill und Seilacher	Do.
Beckamin P682-35	Reichholdt Chemie	Do.
Beetle Resin-38		Do.
Modurit M 4	Casella	Melamine Formaldehyde.
Ciba 286	Ciba	Do.
Paper Resin 605	American Cyanamid Corp.	Do.

The degree of polymerization of the resin and the molecular ratio of the starting materials for the condensation are not critical as far as the sterilization is concerned. As a consequence, it is possible in all instances to select the resin which imparts the most favorable properties after the sterilization, e.g. wet strength, softness and absorption capacity, and also to observe economical considerations.

The sterilizable paper ware may, for example, consist of one or a plurality of similar layers of paper material, e.g. cellulose, tissue containing 0.5–4% by weight of formaldehyde resin. Such material is, for example, suitable for paper handkerchiefs. If a very high moisture absorbing capacity is desired, for example, for bandages, napkins or insulating pads, e.g. 5–10 layers of highly absorbent paper material, such as cellulose wadding may be laid on the cellulose tissue, and these may, if so desired, be covered with one or two layers of absorbent cellulose tissue having a high wet strength due to a suitable content of formaldehyde resin. Such laminated bandages may be cut up into pieces of the desired size. For a bandage this may, for example, be 15 x 30 or 30 x 30 cm.

It is also possible to wrap a few layers of absorbent paper material in one or more layers of cellulose tissue containing a formaldehyde resin. Such a packet may

be used for bandaging wounds, and be fastened in any of the conventional methods, for example, with a closure sheet.

Another feature of the invention is the sterilization of paper waddings of quilts. Such paper waddings may be used in a textile cover which has been separately sterilized. These waddings can solve the problem of hospitals, where sterilization of blankets is required. The conventional woolen blankets, however, are not resistant to repeated sterilization, as they will soon shrink to such an extent as to become useless.

In the embodiments of the invention the cellulose wadding may also contain a formaldehyde resin. It is true that this reduces the moisture absorbing capacity to some extent but it also prevents formation of dust:

Inasmuch as cellulose wadding is apt to be affected by dry-heating above 110° C., paper material containing cellulose wadding is preferably not sterilized above 110° C.

If such a laminated product is heated in a furnace, preferably at 100–110° C., vaporous formaldehyde is released from the formaldehyde resin, which penetrates the whole bandage and kills all germs present. The wet strength of the resin-containing layer is not appreciably reduced by such treatment.

It has been found that the development of formaldehyde upon heating may continue for hours on a stretch, so that a prolonged sterilization is possible. In some cases, e.g. in the case of bandages, it will be necessary for a product that has been sterilized earlier, to be sterilized again, and this may also be effected without deterioration of the wet strength.

After the sterilization the hygienic paper material may be used immediately or it may be kept ready for use or marketed as a sterilized package. In the two last-mentioned cases it is advantageous for the material to

be packaged first in a bacteria-impermeable envelope, which is resistant to the sterilization temperature and then to be sterilized in the envelope.

Examples of suitable envelopes are closed containers of glass or metal, such as steel or aluminum or of thermoplastic materials, such as polypropylene or nylon bags. When using plastics it is of course necessary not to exceed the softening point of the plastic during the dry-heating. An excellent bacteria impermeable envelope is a paper bag or any other well closed paper container or wrapper.

Bacteria impermeable envelopes of the above mentioned kind are well known in the art and need no further description.

As a material for envelopes, paper has the advantage, that it is virtually impermeable to bacteria and yet permeable to gases. This means that the formaldehyde released by the dry heating can escape through the paper. There is thus no danger that sterilized bandages may still contain traces of harmful formaldehyde.

As the formaldehyde resins are entirely stable at the temperature of the human body, there is no danger that a wound treated with a bandage sterilized in accordance with our invention will be irritated by subsequently released formaldehyde. The resins per se do not irritate

the wound, for in the ready product they are bonded to the fibre in the condensed state.

The invention is illustrated by means of the following examples:

Example I

A cellulose tissue web was made from a batch of paper pulp consisting of 40% Bowler bleached sulphate pulp, having a fiber length of about 1 mm., made from hardwood and 60% Wezerhainzer bleached sulphite pulp, having a fiber length of 3-4 mm., made from soft wood. While this pulp was being worked in the beater, there was added to it a quantity of water soluble urea formaldehyde resin sold under the trademark Urecoll K. This resin has a urea formaldehyde ratio of 1:2.5.

The quantity of resin was chosen so as to yield a cellulose tissue with a resin content of 2% by weight. After thorough mixing the pulp was fed to a paper making machine and used in the customary way to produce a cellulose tissue having a weight of 22 g./m.², a dry breaking length in machine direction 850 m. and a wet breaking length of 250 m. During the passage of the web through the paper making machine the cellulose tissue remained in contact with heated rolls for 1.8 sec. This period was sufficient to cure the water soluble resin to form a partially cured water insoluble product which firmly bonds the cellulose fibers together. The finished cellulose tissue had a soft touch and was able to absorb 8 times its own weight of water. Entirely similar materials are obtainable from many commercial sources.

Two sheets of this cellulose tissue were laid upon each other. Upon these were laid six layers of cellulose wadding. These did not contain any resin and had been manufactured from cellulose fibres in a customary way to yield a web with a weight of 8.5 g./m.² and then creped to yield a web of 17 g./m.² Upon these were laid two more sheets of the cellulose tissue and the layered product was cut up into bandages measuring 15 x 30 cm. The thickness of the bandages was approximately 5 mm.

A number of these bandages were rolled up, inserted in a glass tube closed with a polypropylene stopper, heated for one hour at 104° C. and subsequently cooled. Upon examination a sample of these bandages was found not to contain any viable germs. The breaking length in dry, state of the cellulose tissue had increased to 910 m. After 30 minutes immersion in water at room temperature the breaking length was 320 m. The wet strength of the bandages had remained very good and the moisture absorbing capacity had not changed to any appreciable extent.

Example II

From the same packet of 6 layers of cellulose wadding and 4 layers of cellulose tissue as in Example I sheets of 100 x 180 cm. were cut, destined as a wadding for sterilizable quilts. The pieces were packaged in flat condition in a well-closed paper bag made of ordinary wrapping paper and the whole was heated in a furnace for 45 minutes at 105° C. The quilt wadding was entirely sterilized, and could be used in a separately sterilized cover of textile fabric.

Example III

A packet of 10 layers of cellulose wadding was divided into pieces of 30 x 30 cm. with a thickness of approximately 8 mm. These pieces were folded into two layers of cellulose tissue containing 2.5% by weight of melamine formaldehyde resin calculated on the air-dry material. Thereafter the bandages were sterilized by heating for 1½ hours at 100-105° C. After cooling no viable micro-organisms could be isolated from the bandages, and the wet strength and the moisture-absorbing capacity had not changed to any appreciable extent.

The cellulose cloth was made in the same way as described in Example I, except that 2.5% of Madurit M4 was added instead of 2% of Urecoll K. The wet strength of this cellulose cloth was 32% of the dry strength.

Example IV

The operations described in Example I were repeated with the difference that the cellulose tissue contained different kinds of different resins, as appears from the following table. In this table PhF indicates a phenol formaldehyde resin, UF a urea formaldehyde resin and MF melamine formaldehyde resin. The figure under the heading "Ratio" indicates the mol ratio of phenol, urea or melamine to formaldehyde. The molecular weight given is the average molecular weight of the water soluble resin; the quantity of resin is expressed as percent by weight of partially cured resin in the finished but unsterilized cellulose tissue.

Resin	Type	Ratio	Quantity, percent	Break length wet Break length dry	Sterilization results
Urecoll K.-----	UF	1:2.5	2	28	Complete sterility.
Do.-----			1½	24	Do.
Do.-----			1	19	Do.
Madurit M4.-----	MF	2:3	2	32	Do.
Do.-----	MF	2:3	1½	27	Do.
Do.-----	MF	2:3	1	23	Do.

The sterilisation was carried out in all cases by heating for 1 hour at 105° C. in a glass test tube, closed with a plug of cotton wool. The bandages were in each case tested by a standard procedure to show the presence of any visible, micro-organisms. In all cases complete sterility was obtained.

I claim:

1. A method of sterilizing hygienic paper ware comprising preparing moisture absorbent paper material of which at least a part has an enhanced wet strength and includes 0.5-4% by weight based on said part of a partially cured formaldehyde resin distributed therein and adapted for enhancing said wet strength of said paper material, said resin being selected from the group consisting of phenol formaldehyde resins, urea formaldehyde resins and melamine formaldehyde resins, said resin being introduced into the paper pulp during the preparation of the paper material and partially cured to form a resin containing a substantial quantity of $-\text{CH}_2\text{OH}$ groups capable of releasing free formaldehyde on heating, at temperatures from at least about 60° C., enclosing said paper material in a bacteria impermeable envelope capable of resisting a sterilization temperature to be applied thereto, and dry heating the material in said envelope at a temperature within the range of from 60 to 150° C. for at least 30 minutes and sufficiently long to sterilize the paper material by the action of the formaldehyde vapor which is thereby released.

2. A method as claimed in claim 1 comprising dry heating the paper material in said envelope at a tempera-

ture within the range of from 100 to 120° C. for at least 30 minutes.

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