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## DEODORIZATION OF PAPER

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The subject of the present invention is the deodorization of papers containing malodorous substances as a result of the addition to the papers of certain desirable papermaking ingredients.

I have found that papers containing malodorous substances can be deodorized with suitable oxidizing agents so quickly that the paper may be processed as a continuously and rapidly moving sheet, for instance, even while it is still undergoing fabrication at high speed on a paper machine, or as it comes off the paper machine. When the paper contains malodorous substances which react with volatile oxidizing agents such as the halogens or ozone, the continuous web of paper, preferably while moist, can be passed through an atmosphere of the oxidizing agent. In fact, if the paper contains the malodorous substances while undergoing fabrication on the paper machine, the nascent web may be only partially dried and then passed through the oxidizing atmosphere, whereupon the drying operation can be completed. The presence of water in the web promotes the deodorizing reaction when an atmosphere of oxidizing agent of the type of chlorine or other halogens, which are water-soluble, is relied upon for deodorization.

While not limited thereto, my invention can be applied most usefully in the production of papers into which viscose has been incorporated as a papermaking ingredient. Viscose may be used in papers for various reasons, but its association in very small amounts with papers intended for use in toweling is attended by a remarkable precision of the wet strength of the toweling, with little, if any, depreciation in the water-absorptivity of the toweling. For example, when as little as 1% viscose, calculated as cellulose, is added to paper toweling which is otherwise free from sizing or filling ingredients, the toweling undergoes a multifold increase in wet strength (as much as five to seven times, or more), without losing its original capacity for absorbing water. When paper toweling is treated with viscose, however, it assumes an offensive odor, because of the impurities which result either from the regeneration of the cellulose in the viscose, or which are originally present in the viscose. These impurities are largely, if not entirely, sulphur compounds, which may impart a very objectionable odor to the toweling, even when present in the merest traces. In working with viscose as an ingredient for paper toweling, I was bothered greatly by the fact that in some cases the offensive odors were seemingly removed when the viscose solution underwent suitable treatment, for instance, aeration and/or the action of ammonium salts, such as ammonium carbonate, added to the viscose. Although the odoriferous impurities were indeed largely removed from viscose so treated, there were left in these cases traces, which, although overlooked by men who were working with the viscose and at the time the toweling was made, nevertheless were potentially obnoxious, especially when the toweling was packaged, as in the usual roll form, or as interleaved sheets, in a closed container or carton, wherethrough there was little, if any, circulation of air to carry away the obnoxious odors. In other words, the atmosphere of the closed container or carton for the towel package became heavily laden with the odors progressively emitted from the traces of impurities present in the towel package. As is well known, people working in a slightly odoriferous atmosphere may become oblivious to the existence of the odor because of adjustment of the sense of smell thereto. Yet a newcomer may find the atmosphere not only objectionable, but actually sickening. For instance, a dealer who receives a container packed with paper toweling from which an evil odor emanates, at once detects the odor and condemns the toweling. So, too, a fastidious person using the toweling, who is working in a clean atmosphere and is hence sensitive to even slightly bad odor, is also repelled from using the paper toweling, unless it is substantially odorless or free from objectionable odor. While aeration and/or the addition of ammonium salts to viscose before the viscose is incorporated into the paper web and then dried out at elevated temperature removes very nearly all of the odoriferous materials therefrom, there may be, as already in-

dicated, sufficient odoriferous impurities left in the toweling to give rise to complaints by the dealers and users, on account of bad odor.

The process of the present invention not only is simple, inexpensive, and eminently practicable, but can be applied to effect the removal of all vestiges of offensive odor from paper toweling containing viscose, wherefore the most fastidious person can detect no evil odor in the toweling when opening a carton containing one or more towel packages, or when using a single towel. Very important, too, my process accomplishes the desired end without materially detracting from the enhanced wet strength of the toweling or seriously reducing its water absorptivity. In accordance with my process, the web of toweling may be passed through a viscose solution of the desired strength, squeezed free of excess solution, and then dried. By way of illustration, the viscose solution may be one of about ¾% strength in terms of soluble cellulose. The squeezing operation may be controlled to reduce the viscose solution content of the web to a point where the web holds its own weight of solution, and thus has a viscose content in terms of soluble cellulose, based on fiber, similar to that of the impregnating solution, viz., ¾%. The dried viscose-containing web may then be passed through a dilute chlorine solution, say, one containing up to about 0.5% chlorine, then squeezed free of excess solution, and finally dried. The odoriferous or odor-generating substances introduced into the toweling along with the viscose is thereby entirely eliminated. Solutions of other oxidizing agents, such as hypochlorite and sodium or hydrogen peroxide, may be used instead of chlorine water. When a hypochlorite is used, it is preferably the hypochlorite of a highly soluble base, such as sodium, which class of hypochlorite does not deposit difficultly soluble residues in the toweling. An advantage of the deodorizing treatment described is that the toweling need not be washed after treatment with the oxidizing agent, but may be at once redried without noticeable effect upon either its dry or wet strength, or upon its capacity for absorbing water. One may, however, subject the deodorized toweling to a treatment with wash water before the final drying operation, in which case the water-soluble chemicals and reaction products are removed.

The oxidant may be applied to the toweling in a way which is even simpler than that already described. Thus, the viscose-impregnated toweling may, without intermediate drying, be passed through a solution of oxidizing agent, then between a pair of squeeze rolls, and finally dried. In this latter method, the oxidizing solution is preferably slightly stronger than that used in the first-described method, because there is no volatilization of the more volatile sulphur compounds by the heat applied during an intermediate drying operation. In other words, sufficient additional oxidant is used to react with the volatile sulphur compounds, which would otherwise be expelled from the toweling by heat. It is my theory that by my process, not only are the sulphur impurities oxidized in situ in the toweling into colloidal sulphur, which does not interfere materially with water absorption by the toweling, but further, that regeneration of cellulose from the viscose is hastened and made substantially complete on the drier, so that there is very little chance for after-regenerating effects, accompanied by the formation of evil odors in the dried toweling.

When the toweling is passed through viscose solution and then squeezed there is retained in the toweling, as hereinbefore described, about an equal weight of solution containing ¾% viscose based on dissolved cellulose. When the impregnated towel is introduced directly into the oxidizing solution, it immediately absorbs the solution to an extent which depends upon the time of contact and upon the characteristics of the solution, and the characteristics of the fiber comprising the toweling. The maximum amount of oxidizing solution taken up by a kraft towel, for example, may be about 100 to 150% the weight of the fiber. The oxidizing solution mingles in the pores of the sheet with the viscose solution and when a moment later the towel is again passed through squeeze rolls to facilitate drying, the mixed solutions are squeezed out of the pores. Now it is an important and interesting discovery that substantially no appreciable quantities of soluble cellulose or regenerated cellulose are squeezed out of the pores. That is to say, the oxidizing solution precipitates the soluble cellulose within the pores. This precipitation may be due partly to a salting-out effect, partly to a breaking up of the xanthate by oxidation of the sulphur contained in it, or by precipitation of the xanthate, depending upon the type of oxidizing solution used. If it were not for this precipitation within the pores of the towel it would obviously be very wasteful of both viscose and oxident, for more viscose would have to be added, than corresponded to the amount of regenerated cellulose needed in the final towel, the excess being equal to that quantity which would be squeezed out during the second pressing. That the very small quantities of oxidizing agents needed will fix the soluble cellulose within the pores of the fibre, consequently represents an important phase of my invention.

A third mode of procedure, in accordance with my invention depends on the use of an oxidizing atmosphere, rather than an oxidizing solution. In such case, the toweling is impregnated with the viscose solution in

the usual way, is then passed over a bank of drier rolls, and while still moist is passed through an oxidizing atmosphere afforded as by chlorine or other halogen. The toweling thus deodorized is then passed over another bank of drier rolls, by which it is substantially completely dried. The concentration of the halogen in the oxidizing atmosphere, and the time of exposure of the toweling to the oxidizing atmosphere, are regulated so that the toweling issues completely deodorized from the oxidizing atmosphere, ready for final-stage drying. It is easy to regulate the conditions of treatment in the oxidizing atmosphere to effect deodorization of the toweling without injuring the fiber, as a result of oxidation and/or hydrolysis of the cellulose into oxycelluloses, as the deodorizing reaction is evidently quite selective and, as already indicated, proceeds to completion in an exceedingly short period of time. In lieu of an oxidizing atmosphere furnished by chlorine or other halogen, other oxidizing atmospheres, e. g., an ozone-containing atmosphere, may be used.

It is a surprising phenomenon that viscose-containing toweling can be completely and permanently deodorized without being chemically or physically injured, and further, that such deodorization is accomplished even when oxidized impurities are permitted to remain in the toweling. In this connection, it is to be observed that in the manufacture of paper toweling, the manufacturer often employs the strongest available wood pulp, so as to realize the strongest toweling attainable from the wood fiber alone. To this end, kraft pulp, which is the strongest chemical wood pulp, is chosen as the cellulose base. Kraft pulp, however, contains a notable residue of ligneous material, since the kraft process of fiber liberation is less selective on lignocelluloses than are other chemical pulping processes, such as the sulphite process. The tan-colored, raw kraft pulp is customarily used as such, on account of the high bleach usage necessary to whiten such pulp, and the injurious effect of such bleach usage on fiber strength. It is remarkable that, despite the fact that lignin reacts almost instantaneously with an oxidizing solution, especially chlorine water and hypochlorite liquor, nevertheless the desired elimination of odoriferous sulphur residues from kraft toweling can be accomplished through the use of only small quantities of oxidants. In other words, although ligneous matter can be removed selectively from kraft pulp alone with small amounts of chlorine water or equivalent oxidant, yet the reaction of such oxidants upon the sulphur impurities introduced into the pulp by viscose is evidently even more selective and can proceed selectively to completion in the presence of a large excess of ligneous matter. My process, while applicable to paper toweling made from pulp furnishes of a wide variety, is specifically adapted to the intrinsically strong paper toweling fabricated from kraft pulps.

One phase of my invention involves the introduction of the viscose into the paper-making stock in the beater engine, into the stock while it is on its way to the paper machine, or into the stock after it has been formed as a nascent web on the paper machine. In such case, the viscose-containing web, after only partial drying on the paper machine, can be passed through an atmosphere of oxidizing agent which deodorizes the web completely and permanently as hereinbefore described. The deodorized and partially dried web may then be dried to completion. Such a process avoids the necessity for redrying the paper and thus means that my invention can be practised inexpensively and with the simplest kind of apparatus. Thus, the viscose-containing web may be dried on the paper machine to a fiber content of, say, about 65% to 70%, whereupon the partially dried web may be passed through an oxidizing atmosphere. At this stage of dryness, the volatilizable sulphur impurities have been largely expelled by heat and the web may be festooned or otherwise supported without breakage in the oxidizing chamber to permit sufficient time of exposure to the oxidizing atmosphere. At this stage of dryness, however, there is still sufficient moisture in the web to promote a smooth and rapid reaction between a gaseous oxidizing agent, such as chlorine, and the oxidizable, odoriferous impurities present in the web.

When the oxidant is used in solution, I have found that it is best to segregate the oxidizing solution squeezed from the web, immediately after impregnation, from the main bath of oxidizing solution. When the dry web of toweling is dipped in the oxidizing solution, say, in water containing say, .05% chlorine, it may absorb about 2¼ to 3½ times its weight of solution, whereupon it is run through a pair of press rolls adjusted to remove all but, say, its own weight of solution. The solution squeezed from the toweling is substantially devoid of oxidizing agent, having been completely exhausted in the short interval of time between its introduction into the toweling and expulsion of the excess by the press-rolls. The spent oxidizing solution should hence not be directed to the main bath of oxidizing solution, as it would simply contaminate the bath and render the control of the composition of the bath a difficult matter.

As already indicated, the viscose-treated paper toweling may be washed after the oxidizing treatment. A meritorious feature of my process, however, lies in the fact that no such washing is necessary. When wash water is used after the oxidant treatment, no

difficulty is encountered, since not only has the toweling been enhanced in wet strength by the viscose treatment so as to withstand rupture under stress in a bath of wash water, but the viscose has been rendered water-insoluble by the oxidizing treatment, and hence is not leached out by the wash water.

I claim:

1. As an article of manufacture, dried, viscose-treated paper entirely and permanently free from malodors.

2. As an article of manufacture, dried, viscose-treated paper toweling entirely free from evil odors and from substances which generate evil odors.

3. As an article of manufacture, paper toweling treated with about 1% viscose, calculated as soluble cellulose, based on the weight of the dry paper, and completely and permanently freed from malodors.

4. As an article of manufacture, kraft paper toweling treated with viscose and completely and permanently freed from malodors.

5. A step which comprises treating viscose-containing paper with an oxidizing agent to destroy foul odors and odor-generating substances in such paper.

6. A step which comprises treating viscose-containing paper with chlorine water to destroy foul odors and odor-generating substances in such paper.

7. A process which comprises treating viscose-containing paper with an oxidizing agent to destroy foul odors and odor-generating substances in such paper, and washing the paper with water to remove water-soluble products.

8. A process which comprises treating viscose-containing paper with a solution of an oxidizing agent to destroy foul odors and odor-generating substances in such paper, and drying the deodorized paper.

9. A step which comprises treating viscose-containing paper with a gaseous oxidizing agent to destroy foul odors and odor-generating substances in such paper.

10. A process which comprises treating wet, viscose-containing paper with a gaseous oxidizing agent to destroy foul odor and odor-generating substances in such paper, and drying the deodorized paper.

11. A process which comprises treating the wet viscose-containing paper with chlorine gas to destroy foul odor and odor-generating substances in such paper, and drying the deodorized paper.

12. In the manufacture of viscose-treated papers permanently free from evil odors, those steps which comprise running papermaking pulp off on a papermaking machine as a continuous web of paper, progressively treating the web as it comes from the machine with a viscose solution, progressively treating the viscose-containing web with an oxidizing solution to destroy foul odor and odor-generating substances in the web, and progressively drying the deodorized web.

13. A process which comprises only partially drying a nascent wet web of paper associated with viscose, passing the partially dried web through an atmosphere of oxidizing gas to destroy foul odor and odor-generating substances in the web, and completely drying the web.

14. A process which comprises drying a nascent wet web of paper associated with viscose to a cellulose content of about 65% to 70%, passing the partially dried web through an atmosphere of oxidizing gas to destroy foul odor and odor-generating substances in the web, and completely drying the web.

15. A process which comprises only partially drying a nascent wet web of paper associated with viscose, passing the partially dried web through an atmosphere of chlorine gas to destroy foul odor and odor-generating substances in the web, and completely drying the web.

16. A process which comprises treating a web of waterleaf paper with a viscose solution, drying, treating the dried, viscose-containing paper with a solution of an oxidizing agent to destroy foul odor and odor-generating substances in the web, and redrying.

17. A process which comprises treating a web of waterleaf paper with a viscose solution, partially drying, treating the partially dried, viscose-containing paper with a water-soluble, gaseous oxidizing agent to destroy foul odor and odor-generating substances in the paper, and drying to completion.

18. A process which comprises treating a web of cellulose with a viscose solution, treating the viscose-containing paper with a solution of oxidizing agent to destroy foul odor and odor-generating substances in the web, squeezing the web to remove excess solution, and drying.

19. A process which comprises progressively treating a continuous web of cellulose with a viscose solution, progressively passing the viscose-containing web through a bath of oxidant solution to destroy foul odor and odor-generating substances in the web, squeezing the web to remove excess solution, segregating the removed solution from the bath of oxidant, and progressively drying the web.

20. A process which comprises progressively impregnating a continuous web of paper as it is proceeding at a high rate of speed with a viscose solution, passing the impregnated web while it is wet through a chlorine gas atmosphere wherein it remains for only an exceedingly short period of time, and progressively drying the chlorinated web.

In testimony whereof I have affixed my signature.

MILTON O. SCHUR.