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CHLORITE BLEACHING IN THE PRESENCE OF A NITROGEN COMPOUND EMPLOYED AS A CORROSION INHIBITOR

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This invention relates to a bleaching composition non-corrosive to metallic surfaces. In a specific aspect, this invention relates to a process for the bleaching of cellulose and cellulose derivatives with a chlorite bleaching agent and to the composition of matter employed in the bleaching operation. In a more specific aspect, this invention relates to a process for inhibiting the corrosive action of chlorite bleaching agents on metallic reaction chambers in a cellulose acetate bleaching process and to the noncorrosive bleaching composition employed in the bleaching operation.

Cellulose derivatives, for example, cellulose ethers and esters, and, more particularly, cellulose acetate, are employed in high temperature operations, such as molding, for the formation of a wide variety of articles, and in such high temperature operations it is essential that the cellulose derivative have a high thermal color stability in order that the articles resulting from the high temperature process can be substantially colorless. It has recently been found that cellulose derivatives that have been bleached with a chlorite, for example, an alkali metal or alkaline earth metal chlorite, have a thermal color stability higher than that of similar cellulose derivatives that have been bleached with other known bleaching agents. In carrying out the bleaching process with the chlorite bleaching agent, an aqueous slurry of the cellulose derivative is formed and the pH of the slurry is adjusted with an acid to obtain a pH lower than 7. The cellulose derivative is then bleached by introduction of the chlorite bleaching agent. Various acids can be used for the pH adjustment, but it has been found that the acidic bleaching medium containing the chlorite bleaching agent has a corrosive action upon the metallic reaction chambers, particularly those constructed of ferrous metal, such as stainless steel, both in the liquid phase and in the vapor phase. The corrosiveness of the bleaching medium while in the liquid phase has been overcome by employing phosphoric acid for pH adjustment. However, the use of phosphoric acid does not solve the problem of inhibiting the corrosion in the vapor phase above the liquid bleaching medium.

A similar problem is encountered in the bleaching of cellulosic materials, such as cotton linters, wood pulp, bagasse, and the like, with chlorite bleaching agents or chlorine dioxide. These bleaching agents are corrosive to the metallic surfaces of the reaction chambers, and obviously a method for inhibiting the corrosive nature of these bleaching agents is highly desirable.

It is an object of this invention to provide a novel process for the treatment of cellulose and cellulose derivatives.

It is another object of this invention to provide a novel process for bleaching cellulose and cellulose derivatives with a chlorite bleaching agent and for inhibiting the corrosive nature of the bleaching agent.

It is another object of this invention to provide a novel process for the bleaching of cellulose esters with a chlorite bleaching agent.

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It is another object of this invention to provide a novel bleaching composition containing either chlorine dioxide or a chlorite bleaching agent and a corrosion inhibitor.

It is another object of this invention to provide a novel process for inhibiting the corrosive action of metal chlorites on metallic reaction chambers in a cellulose acetate bleaching process.

It is a further object of this invention to provide a novel noncorrosive chlorite-containing bleaching composition.

In accordance with this invention, it has been found that the corrosive action of an aqueous solution of a water-soluble inorganic chlorite or chlorine dioxide bleaching agent upon metal surfaces, particularly ferrous metal surfaces, can be inhibited by adding to such an aqueous solution a nitrogen compound, having at least one hydrogen atom attached to the nitrogen atom, that is at least slightly hydrolyzable in said solution to yield ammonia or a similarly basic volatile derivative of ammonia.

Example 1

One hundred grams, on a dry basis, of cellulose acetate that had been precipitated from its reaction dope and washed substantially free of acid was slurried in an open stainless steel vessel in 1500 ml. of water containing 6 ml. of a bleaching solution of the following composition:

9 g. sodium chlorite (80% assay)
5.3 g. ammonium chloride
100 ml. water

The slurry was stirred and heated 1.75 hours at 75–100° C. after which it was thoroughly washed and dried. When dissolved as a 20% solution in 9:1 acetone-ethanol, the bleached cellulose acetate was found to have a color of 118 Hazen. The unbleached cellulose acetate had a color of 272 Hazen. No staining or corrosion of the stainless steel vessel occurred.

Example 2

Four hundred grams (dry basis) of cellulose acetate that had been precipitated from its reaction dope and washed substantially free of acid was slurried in 8 liters of water. The slurry was heated to 90–95° C. while agitating. Then 1½ ml. of a stock bleach solution per liter of water was added and stirring was continued for 4 hours. The stock bleach solution had the following composition:

Sodium chlorite	9 g. (80% assay).
Ammonium sulfate	6.6 g.
Water	100 ml.

After completion of the bleach treatment, the cellulose acetate was thoroughly washed and dried. No corrosion of the stainless steel vessel occurred. The unbleached cellulose acetate had a color of 95 Hazen when dissolved in a 20% solution in 9:1 acetone-ethanol. The bleached cellulose acetate had a color of 57 Hazen.

In another run, a similar amount of cellulose acetate was bleached in the manner described above with a bleaching solution having the following composition:

Sodium chlorite	9 g. (80% assay).
Ammonium phosphate	4.4 g.
Water	100 ml.

The bleached cellulose acetate had a color of 54 Hazen. No corrosion or staining of the stainless steel vessel occurred in this run.

Example 3

A series of runs for bleaching cellulose acetate was carried out in the following manner:

Run 1.—Four hundred grams (dry basis) of cellulose acetate that had been precipitated from its reaction dope,

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washed substantially acid-free, stabilized by boiling in water at 14–18 p. s. i. containing 0.06% acetic acid for one hour, was slurried in 8 liters of water. The slurry was heated to 95° C. and 0.8 g. of sodium chlorite and 0.2 g. of ammonium sulfate were added. The temperature was maintained substantially constant, and the slurry was stirred for 4 hours. After bleaching, the cellulose acetate was thoroughly washed.

Run 2.—This run was similar to run 1 except that 0.6 g. of ammonium sulfate was used instead of 0.2 g. of ammonium sulfate.

Run 3.—This run was similar to run 1 except that the amount of ammonium sulfate was increased to 1.2 g.

Run 4. This run was similar to run 1 except that the cellulose acetate was dried after stabilizing and washing without undergoing bleaching.

The following colors were observed in the various runs using a 20% solution of cellulose acetate in 9:1 acetone-ethanol:

Run	Solution Color
1.....	23 Hazen.
2.....	10 Hazen.
3.....	23 Hazen.
4.....	110 Hazen.

No corrosion or staining of the stainless steel vessel occurred in the various runs.

Example 4

Specimens of Type 316 stainless steel were etched with hydrochloric acid to give a matte surface and then thoroughly washed. After weighing, the respective test pieces were suspended in the vapor phase above boiling test solutions under reflux having the following compositions:

	Solution	
	A	B
Water, ml.....	200	200
Sodium chlorite, g. (80% assay).....	0.4	0.4
Ammonium sulfate, g.....		0.3
Phosphoric acid, ml.....	0.1	

The averaged rates of corrosion for seven determinations were 0.032 inch per year for the bleach solution acidified with phosphoric acid and 0.0003 inch per year for the ammonia-inhibited bleach solution.

Example 5

Forty-five hundred pounds of cellulose acetate were slurried in about five times its weight of water in a stainless steel vessel. The slurry was heated to 90° C. while agitating. Four pounds of sodium chlorite (80% assay) and 3 pounds of ammonium sulfate dissolved in 2 gallons of water were added to the slurry. The charge was then heated to about 95° C. and maintained at that temperature for 4 hours with agitation. At the completion of the bleach, the cellulose acetate was thoroughly washed with water. No chlorine dioxide or ammonia vapors were detected and no corrosion of the vessel was observed either from the liquid phase or from the vapor phase.

In the above examples, the color of the cellulose acetate can be determined by preparing a solution of 50 grams of dried cellulose acetate dissolved in 20 grams of denatured ethanol and 180 grams of acetone. The solution is placed in a bottle similar to those holding various Hazen color standards and compared visually. Hazen standards are prepared by dissolving 1.245 grams of potassium chloroplatinate and 1.0 gram of cobalt chloride in distilled water containing 100 ml. of 37% hydrochloric acid and

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diluting to 1000 ml. This solution is No. 500 Hazen. Other solutions are prepared from the stock solution as follows:

Hazen Standard No.	ml. No. 500 Standard	ml. Distilled Water
500.....	100	0
400.....	80	20
300.....	60	40
200.....	40	60
100.....	20	80
50.....	10	90
40.....	8	92
30.....	6	94
20.....	4	96
10.....	2	98
0.....	0	100

The corrosion-inhibiting compounds employed in practicing this invention are nitrogen compounds having at least one hydrogen atom attached to the nitrogen atom. Ordinarily, ammonia conveniently in the form of an aqueous solution or ammonium salts can be used. For example, ammonium acetate, ammonium chloride, the ammonium phosphates, ammonium sulfate, ammonium nitrate, and similar ammonium salts, can be used. The ammonium salts of inorganic acids, such as mineral acids, are generally preferred mainly because of their availability and economy. However, primary and secondary amines are also suitable for corrosion inhibition. Such amines are, for example, aniline, morpholine, toluidene, methyl aniline, benzylamine, diphenylamine, diamylamine, methylamine, ethylamine, diethanolamine, and the like. Also, acid amides, such as acetamide, formamide, butyric amide and the various monosubstituted alkyl and aryl amides can be used. Similarly, compounds of the urea type, such as urea, methylurea, ethylurea, diphenylurea, diethylurea, the urethanes, and other substituted ureas or thioureas can be used. Also, guanidines, substituted guanidines, and the like are similarly suitable. It will be understood that in referring to the ammonia, amine or other nitrogen compound having a hydrogen atom attached to the nitrogen atom such nitrogen compound may be in the basic form or in the form of a salt either before addition to the bleaching solution or after such addition.

The nitrogen-containing corrosion inhibiting compound that is used should be sufficiently hydrolyzable in the bleaching medium to yield ammonia or another basic, volatile compound at the conditions employed for bleaching or the nitrogen-containing corrosion inhibiting compound itself, basic in nature, should be substantially volatile at the bleaching conditions employed. Furthermore, the nitrogen-containing corrosion inhibiting compound or its hydrolysis residue should not be susceptible to oxidation by the chlorite bleaching agent. Otherwise, the bleaching activity of the chlorite is either impaired or destroyed.

In the above specific examples which are illustrative of this invention, sodium chlorite was used as the bleaching agent. Sodium chlorite is the preferred bleaching agent and it is available commercially. However, the invention can be practiced by using either chlorine dioxide or chlorite bleaching agents other than sodium chlorite. Typical examples of other chlorites are ammonium chlorite and the alkali metal and alkaline earth metal chlorites such as potassium chlorite, calcium chlorite, magnesium chlorite, barium chlorite, and the like.

The bleaching process of this invention is useful for the bleaching of either cellulose or cellulose derivatives. The cellulose may be in the form of a textile material or in the form of a cellulose fiber such as that obtained from wood or cotton linters. The cellulose derivatives are usually of the cellulose ester or ether type. Typical cellulose derivatives are methyl cellulose, ethyl cellulose, carboxymethylcellulose, cellulose acetate, cellulose propionate, cellulose butyrate, and the like. Also, mixed ester, mixed ether and ether-ester derivatives can be

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bleached in accordance with this invention. For example, cellulose acetate propionate, cellulose acetate butyrate, carboxymethyl hydroxyethyl cellulose, acetylated hydroxyethyl cellulose, and the like are within the scope of this invention. In its preferred form, the invention is applied to the bleaching of cellulose esters, preferably cellulose acetate, with sodium chloride, and the details of the invention will be described with reference to such a process.

When cellulose or a water-insoluble cellulose derivative is bleached in accordance with this invention, water can be used as a medium for slurring the material to be bleached. When the cellulose derivative is water soluble, such as sodium carboxymethyl-cellulose, inert water-miscible organic liquids which are nonsolvents for the cellulose derivative can be used. Typical examples are the lower aliphatic alcohols, for example, methyl alcohol, ethyl alcohol, isopropyl alcohol, tertiary butyl alcohol, and the like, and aqueous solutions of such alcohols. Other organic liquids that can be used are dioxane, tetrahydrofuran, the diethyl ether of ethylene glycol, and the like.

The cellulose esters employed in practicing this invention can be prepared by any of the known methods. A typical method for preparing these cellulose esters will be set forth by describing a method for preparing cellulose acetate. One method of preparing cellulose acetate involves the preparation of a cellulose mix by spraying cotton linters with glacial acetic acid. An acetylation mix is separately prepared by mixing together acetic anhydride, methylene chloride and catalytic amounts of zinc chloride and perchloric acid. This latter mix and the cellulose mix are combined and agitated for a period of time sufficient to effect the desired acetylation. At the end of this period of time the reaction is arrested by the addition of aqueous acetic acid, and, either without hydrolysis or hydrolyzing the product to a desired degree of combined acetic acid, the catalyst is then neutralized with aqueous sodium acetate. The methylene chloride is then removed by distillation and aqueous acetic acid is added until a state of incipient precipitation is reached. Precipitation is then completed by the addition of water and the product is purified by water washing and it is then air dried. Another method of preparing cellulose acetate involves a procedure similar to that described above, but in place of the zinc chloride-perchloric acid catalyst a sulfuric acid catalyst is used. Either of these methods or any other method known for producing cellulose esters is within the scope of this invention.

In practicing the invention, the cellulose ester in granular or flake form is suspended in water using from about 5 to 20 parts by weight of water per part of cellulose ester. It is preferred that the cellulose ester be substantially free of acid in order that the resulting slurry will be substantially neutral. The resulting slurry is heated to a temperature within the range of 70–150° C., and a pressure sufficient to maintain the water in the liquid phase is employed. The chlorite bleaching agent is then added to the slurry in the form of an aqueous solution, but in some instances it may be found desirable to employ the chlorite in a solid form. The quantity of chlorite employed is usually within the range of 0.07–0.6% by weight based on the dry weight of the cellulose ester. The corrosion inhibitor is also added to the slurry in order to inhibit the corrosion normally caused by the chlorite bleaching agent. The amount of corrosion inhibitor generally used is within the range of 0.02–0.9% by weight based on the dry weight of the cellulose ester. Ordinarily, the desired bleaching can be obtained in a period of about 1–4 hours. During this period of time the slurry is agitated to insure adequate contacting of the cellulose ester and the bleaching agent, and at the end of this time the cellulose ester is drained and washed thoroughly with water.

If desired, this invention can be employed to bleach a

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cellulose ester at any point in the process for producing such ester subsequent to washing the ester substantially free of acid. Usually, in such a process, the bleaching is carried out subsequent to the precipitation of the cellulose ester from the reaction dope and after the cellulose ester has been washed free of acid. However, if desired, the cellulose ester can be prepared as a solid in the manner described above, and at a subsequent time an aqueous slurry of the acid-free ester can be prepared and the cellulose ester in this slurry is bleached in accordance with this invention.

One of the outstanding features of this invention is the inhibition of the corrosive activity of the chlorite bleaching agent while the bleaching agent is in the liquid phase of the bleaching medium. This corrosive nature has been inhibited by other methods in the prior art. However, that prior art did not solve the problem of inhibiting the corrosive nature of the vapor phase above the bleaching medium. When this invention is practiced, the bleaching medium is substantially neutral and consequently the formation of corrosive chlorine dioxide is minimized. In addition, the ammonium salt in the bleaching medium decomposes or hydrolyzes to form gaseous ammonia which passes into the vapor phase above the bleaching medium, and in that vapor phase the ammonia prevents corrosion by any chlorine dioxide that may have been formed and evolved from the bleaching medium. In the prior art procedures, the presence of the gaseous chlorine dioxide in the vapor phase presented a rather vexing problem. The chlorine dioxide not only corroded the reaction vessel but it also tended to form a rust or stain which sometimes caused discoloration of the cellulose or cellulose derivative undergoing bleaching. When this invention is practiced, the corrosion of the reaction vessel, as well as the discoloration of the cellulose or cellulose derivative by the stained reaction vessel, is prevented.

Also, in prior art procedures employing chlorite bleaching agents, the problem of chlorine dioxide fumes from the bleaching process caused considerable difficulty. The chlorine dioxide evolved from such a process is extremely hazardous and toxic. Ordinarily, it was necessary to install special equipment in order to prevent the dissemination of such chlorine dioxide into the atmosphere. However, when this invention is practiced, no such problem is encountered. In the first place, the absence of acidity in the bleaching medium tends to decrease the amount of chlorine dioxide that is formed. The small amount of chlorine dioxide that is formed appears to become tied up in some way either chemically or otherwise with the ammonia in the vapor phase above the bleaching medium. It has been observed that during the practice of this bleaching process no fumes of either chlorine dioxide or ammonia can be detected. Consequently, there is no need for installation of special equipment to prevent fumes from this process from spreading into the atmosphere.

The bleaching medium employed in this invention contains both the chlorite bleaching agent and the nitrogen-containing corrosion-inhibiting agent. Both compounds can be added to the slurry containing the cellulose ester separately. In some instances, it may be desirable to mix the two compounds in a concentrated solution or master batch prior to addition to the slurry containing the cellulose ester. When the latter procedure is employed, the chlorite and the nitrogen-containing compound should be kept in contact with each other in the concentrated solution for only a relatively short period of time. It has been noted that when the chlorite and the nitrogen-containing compound are in contact with each other in a concentrated state ammonia is evolved from the solution. This results in a loss of effectiveness by the nitrogen-containing compound, and in time the bleach solution will tend to evolve chlorine dioxide. When this occurs, the bleach solution is no longer inhibited against corrosion of the reaction vessel and other metallic surfaces.

What I claim and desire to protect by Letters Patent is:

1. The method for bleaching a material selected from the group consisting of cellulose and cellulose derivatives and for inhibiting corrosion during said bleaching which comprises contacting said material with between about 0.07% and about 0.6% by weight, based on the dry weight of said material, of a water-soluble inorganic chlorite at an elevated temperature between about 70° C. and about 150° C. in a substantially neutral slurring medium containing between about 0.02% and about 0.9% by weight, based on the dry weight of said material, of a nitrogen compound, having at least one hydrogen atom attached to the nitrogen atom, and substantially inert to said chlorite, which hydrolyzes at least slightly in said slurring medium to release a volatile basic nitrogen compound of the group consisting of ammonia and ammonia derivatives from said slurring medium at said elevated temperature.

2. The method according to claim 1 wherein the nitrogen compound in the slurring medium is acetamide.

3. The method according to claim 1 wherein the nitrogen compound in the slurring medium is diphenylamine.

4. The method according to claim 1 wherein the nitrogen compound in the slurring medium is morpholine.

5. The method according to claim 1 wherein the nitrogen compound in the slurring medium is urea.

6. The method of bleaching a cellulose derivative and for inhibiting corrosion during said bleaching which comprises contacting said cellulose derivative with between about 0.07% and about 0.6% by weight, based on the dry weight of said cellulose derivative, of a water-soluble inorganic chlorite at an elevated temperature between about 70° C. and about 150° C. in a substantially neutral aqueous medium containing between about 0.02% and about 0.9% by weight, based on the dry weight of said cellulose derivative, of an ammonium salt of an inorganic acid that reacts to release ammonia from said medium at said elevated temperature.

7. The method for bleaching a cellulose ester and for inhibiting corrosion during said bleaching which comprises contacting said cellulose ester with between about 0.07% and about 0.6% by weight, based on the dry weight of said cellulose ester, of a water-soluble inorganic chlorite selected from the group consisting of alkali metal and alkaline earth metal chlorites at an elevated temperature between about 70° C. and about 150° C. in a substantially neutral aqueous medium containing between about 0.02% and about 0.9% by weight, based on the dry weight of said cellulose ester, of an ammonium salt of a mineral acid that reacts to release ammonia from said medium at said elevated temperature.

8. The method for bleaching a cellulose acetate and for inhibiting corrosion during said bleaching which comprises contacting said cellulose acetate with between about 0.07% and about 0.6% by weight, based on the dry weight of said cellulose acetate, of a water-soluble inorganic chlorite of the group consisting of alkali metal and alkaline earth metal chlorites at an elevated temperature between about 70° C. and about 150° C. in a substantially neutral aqueous medium containing between about 0.02% and about 0.9% by weight, based on the dry weight of said cellulose acetate, of an ammonium salt of a mineral acid that reacts to release ammonia from said medium at said elevated temperature.

9. The method for bleaching a cellulose acetate and for inhibiting corrosion during said bleaching which comprises contacting said cellulose acetate with from 0.07 to 0.6% by weight of sodium chlorite based on the dry weight of said cellulose acetate at an elevated temperature between about 70° C. and about 150° C. in a substantially neutral aqueous medium containing ammonium sulfate in an amount within the range of 0.02 to 0.9% by weight based on the dry weight of said cellulose acetate.

10. The method for bleaching a cellulose acetate and

for inhibiting corrosion during said bleaching which comprises contacting said cellulose acetate with sodium chlorite in an amount within the range of 0.07 to 0.6% by weight based on the dry weight of said cellulose acetate at a temperature within the range of 70–150° C. and for a period of time within the range of 1–4 hours in a substantially neutral aqueous medium containing from 5 to 20 parts by weight of water per part of cellulose acetate and ammonium sulfate in an amount within the range of 0.02–0.9% by weight based on the dry weight of said cellulose acetate.

11. An aqueous substantially neutral noncorrosive bleaching medium comprising, in addition to water, a water-soluble inorganic chlorite and a nitrogen compound, having at least one hydrogen atom attached to the nitrogen atom and substantially inert to said chlorite, which hydrolyzes at least slightly in said medium to release a volatile basic nitrogen compound of the group consisting of ammonia and ammonia derivatives from said medium at an elevated temperature between about 70° C. and about 150° C.

12. An aqueous substantially neutral noncorrosive bleaching medium comprising, in addition to water, a water-soluble inorganic chlorite and a nitrogen compound, having at least one hydrogen atom attached to the nitrogen atom, and substantially inert to said chlorite, which hydrolyzes at least slightly in said medium to release ammonia from said medium at an elevated temperature between about 70° C. and about 150° C.

13. An aqueous substantially neutral noncorrosive bleaching medium comprising, in addition to water, a water-soluble inorganic chlorite and an ammonium salt of an inorganic acid that reacts to release ammonia from said medium at an elevated temperature between about 70° C. and about 150° C.

14. An aqueous substantially neutral noncorrosive bleaching medium comprising, in addition to water, a water-soluble inorganic chlorite selected from the group consisting of alkali metal and alkaline earth metal chlorites and an ammonium salt of a mineral acid.

15. An aqueous substantially neutral noncorrosive bleaching medium comprising, in addition to water, sodium chlorite and ammonium sulfate.

16. An aqueous substantially neutral noncorrosive medium for bleaching cellulose acetate which comprises, in addition to water, sodium chlorite in an amount within the range of 0.07 to 0.6% by weight based on the dry weight of the cellulose acetate to be bleached and ammonium sulfate in an amount within the range of 0.02 to 0.9% by weight based on the dry weight of the cellulose acetate to be bleached.

17. The method according to claim 1 wherein the nitrogen compound in the slurring medium is ammonium sulfate.

18. The method of bleaching a material of the group consisting of cellulose and cellulose derivatives and for inhibiting corrosion during said bleaching which comprises contacting said material with between about 0.07% and about 0.6% by weight, based on the dry weight of said material, of a water-soluble inorganic chlorite at an elevated temperature between about 70° C. and about 150° C. in a substantially neutral slurring medium containing between about 0.02% and about 0.9% by weight, based on the dry weight of said material, of an ammonium salt that reacts to release ammonia from said medium at said elevated temperature.

19. An aqueous substantially neutral noncorrosive bleaching medium comprising, in addition to water, a water-soluble inorganic chlorite and an ammonium salt that reacts to release ammonia from said medium at an elevated temperature between about 70° C. and about 150° C.

(References on following page)

2,810,717

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References Cited in the file of this patent

UNITED STATES PATENTS

1,903,287	Cox	Apr. 4, 1933
1,954,729	Drefus	Apr. 10, 1934
2,126,851	Whitehead	Aug. 16, 1938
2,694,060	Grassie	Nov. 9, 1954

10

FOREIGN PATENTS

507,997 Canada Dec. 7, 1954

OTHER REFERENCES

5 The Paper Industry, September 1954 (pages 576 and 577 relied on).