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(71) Applicant: **L'AIR LIOUIDE, SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE**
75, Ouai d'Orsay
F-75321 Paris Cédex 07 (FR)

(72) Inventor: **Kogan, Jack**
9300 Bennett
Skokie,
Illinois, 60203 (US)
Inventor: **Muguet, Michel**
Domaine de Port Royal,
2 rue de l'Etang
F-78960 Voisins le Bretonneux (FR)

(74) Representative: **Robson, Fiona Susan et al**
L'Air Liquide,
Service Brevets et Marques,
75, quai d'Orsay
F-75321 Paris Cédex 07 (FR)

(54) **Method of inactivating catalase enzyme.**

(57) Provided is a process for destroying the catalase content of a substance or material. The process comprises contacting the substance or material with ozone for a period of time sufficient to destroy the catalase enzyme. The amount of ozone charged to the substance or material is generally in the range of from about 0.01 to 0.15 wt. %, based upon the weight of the substance or material. The process is most particularly applicable to the treatment of a catalase contaminated fibrous pulp which is to be subjected to a hydrogen peroxide bleaching treatment.

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BACKGROUND OF THE INVENTION

The present invention relates to a method useful in overcoming the detrimental effects associated with the presence of catalase enzyme in pulp. More particularly, the present method effectively destroys the catalase enzyme associated with fibrous, e.g., cellulosic, pulp so as to make any subsequent peroxide bleaching step more efficient.

The presence of catalase enzyme in pulp furnishes is well documented. See, for example, "Recent Progress In DeInked Pulp Bleaching", G. Galland, E. Bernard, Y. Vernoe, PIRA, Paper and Board Division Conference on New Developments in Wastepaper Processing and Use, Feb. 28 - March 2, 1989; "Progress in Bleaching Recovered Paper Pulps", G. Galland, Y. Vernoe, M. Dubreuil, L. Bourson, Progress in Paper Recycling, November 1992, p. 20-30; and, "Using Catalase Activity to Measure Microbiological Activity In Pulp and Paper Systems", D.Y. Prasul, Tappi Journal, January 1989, p. 135, 137. The catalase enzyme is believed to be released as part of the metabolic activity of aerobic microorganisms.

Microbiological organisms (contaminants) enter pulp and paper mill systems either through fresh water, incremental reuse of white water or by air. The fibrous and nonfibrous furnish in the presence of other chemicals serve as an abundant source of nutrients for the rapid propagation of microorganisms. Bacteria and fungi seek out these ideal environmental conditions for their growth. In addition, mill temperatures and pH ranges also encourage the rapid incubation of bacteria and fungi.

The enzyme catalase is generally present in all aerobic living systems, for as mentioned above, it is a product of the metabolic activity of aerobic microorganisms. The accumulation of microorganisms, therefore, often leads to limited bleaching efficiency of pulp, particularly recovered paper pulps, due to the presence of the catalase enzyme. The presence of the catalase enzyme is one of the known key factors in limiting the bleaching efficiency of pulps where the bleaching is achieved through the use of hydrogen peroxide, as the enzyme rapidly decomposes the hydrogen peroxide. Brightness is often one of the main criteria of pulp quality, so the bleaching step is an essential step in the upgrading treatment. Disappointing results in the bleaching step can therefore result in poor pulp quality as the desired brightness is not obtained.

Two methods have been suggested to prevent catalase related difficulties in a paper mill. The first consists of keeping the entire system clear of biological development. However, if the pulp being used is itself contaminated with catalase, steps must be taken to destroy the catalase. Thus, the second method involves destroying catalase before the pulp is bleached.

To destroy the catalase, two specific treatments of the pulp (prior to bleaching) have been suggested. See, for example, "Recent Progress in DeInked Pulp Bleaching", by G. Galland, E. Bernard, and Y. Vernac, discussed above. Since catalase is very sensitive to heat, it is irreversibly destroyed at a temperature higher than 70 °C. Thus, thermal pretreatment of the pulp contaminated with the catalase at temperatures such as 80 °C to 90 °C have been suggested. The second treatment that has been suggested involves chemical pretreatment of the pulp with sodium hypochlorite, which is generally accomplished by introduction of the sodium hypochlorite in the pulp prior to bleaching.

While the two foregoing procedures have found some success in destroying catalase and improving the results of any subsequent bleaching step, a safer and more energy efficient process would be welcome. For example, the hypochlorite treatment can cause some environmental concerns relating to the use of a chlorinated product. The thermal treatment requires the use of temperatures up to about 80 °C - 90 °C, involving large expenditures of energy. Recycled paper mills in fact can have difficulties in achieving the required temperatures due to limitations in their steam production capabilities. To provide a more energy efficient and environmentally friendly process for eliminating the catalase contamination of pulp would therefore be of great benefit to the industry.

The use of ozone as a bleaching agent for pulp, and particularly non-cellulosic pulps, is known. See, for example, "Bleaching Deinked Pulp With Ozone" by Jack Kogan and Michel Muguet, Progress in Paper Recycling, November, 1992. The use of ozone in the decolorizing and defluorescing of used paper in a recycling process has also been suggested in Japanese Kokai 3199477.

In German patent application 3001862, published July 23, 1981, there is disclosed a process for the production of raw material for making paper from waste paper. In the process, the waste paper itself is treated with a gaseous disinfecting agent, such as ozone. Subsequent to the treatment, the waste paper is subjected to a recycling procedure, for example, involving solvent treatment and fibrillation. The water paper, due to its contact with household garbage, is generally strongly contaminated with bacteria and microorganisms. The use of the disinfectant agent destroys the bacteria and microorganisms to permit odor free, safe subsequent handling of the paper.

The paper industry continues to struggle, however, with the problem of catalase contamination. In particular, an efficient and effective method for destroying the catalase contamination of pulp

would greatly benefit the industry.

Accordingly, one object of the present invention is to provide a novel process for destroying the catalase enzyme.

Yet another object of the present invention is to provide an efficient and effective process for treating pulp contaminated with the catalase enzyme.

Yet another object of the present invention is to provide a more efficient process for the bleaching of pulp using hydrogen peroxide as a bleaching agent, which process includes a pretreatment of the pulp to destroy any catalase enzyme contamination.

These and other objects of the present invention will become apparent upon a review of the following specification, the Figures of the Drawing, and the claims appended thereto.

SUMMARY OF THE INVENTION

In accordance with the foregoing objectives, provided herewith is a process for destroying the catalase content of a substance or material. The process comprises contacting the substance or material with ozone for a period of time sufficient to destroy the catalase enzyme. The amount of ozone charged to the substance or material is generally in the range of from about 0.01 to 0.15 wt. %, and most preferably in the range of from about 0.05 to 0.15 wt. %, based upon the dry weight of the substance or material. The process is most particularly applicable to the destruction of catalase contained in fibrous pulp, but can also be employed to destroy the catalase contained in, for example, water.

In a preferred embodiment, the present invention relates to a process for bleaching pulp which comprises first pretreating the pulp with ozone for a period of time sufficient to destroy the catalase enzyme contaminating the pulp, and then conducting a hydrogen peroxide bleaching step on the pretreated pulp. The result is a much improved bleached pulp product exhibiting relatively improved brightness in comparison with an untreated product.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 of the Drawing is a graphical depiction of the hydrogen peroxide decomposition which occurs in the presence of catalase with and without the use of an ozone treatment in accordance with the present invention.

Figure 2 of the Drawing is a graphical depiction of the brightness achieved in a pulp by use of a hydrogen peroxide bleaching step with and without the ozone pretreatment step of the present invention.

Figure 3 of the Drawing is a graphical depiction of the brightness achieved by the bleaching of a pulp furnish, with different amounts of ozone being added to deactivate a particular amount of catalase present in the furnish.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention relates to a process for destroying the enzyme catalase which is "contaminating" a substance or material. In part, the present invention is based on the recognition and discovery that ozone can be used efficiently and safely to destroy the catalase enzyme, particularly when the catalase enzyme contaminates fibrous pulp. The water which is used in the mill can be a source of catalase contamination, and has also been found suitable for treatment with ozone in conjunction with the present invention to destroy any catalase contamination that may exist. After subsequently treating the water, the water can be safely used with the pulp prior to or during the bleaching step with hydrogen peroxide.

The pulp which is treated in accordance with the present invention can be any pulp known for making sheet material. The pulp can be a cellulosic containing pulp, such as a virgin mechanical pulp or a recycled pulp. The pulp can also be a wood-free pulp such as a virgin chemical pulp, or a wood-free recycled pulp. One of the important advantages of the present invention is that the amount of ozone employed for the treatment of the pulp to destroy the catalase is insufficient to degrade the fibrous pulp. This is of particular importance in the treatment of cellulose containing pulps. Thus, the present invention can be applied to all pulps. The present invention, however, has been found to have particular applicability in the treatment of thermo-mechanical pulp, which is generally bleached with hydrogen peroxide.

Ozone is generally produced by electrical discharge from pure oxygen or from purified air. There are many advantageous ozone generation systems which use oxygen as the feeding gas. Such systems are highly efficient, of relatively small size and flexible enough to produce ozone according to variable demands. Accordingly, the ozone gas used in connection with the practice of the present invention can be easily supplied on site according to mill requirements and plant configurations, if so desired.

Once the ozone is produced, the ozone gas (or mixture of ozone and oxygen) is injected into a reactor which contains the pulp to be treated. The reactor can be any suitable container having an inlet and outlet for the ozone and an inlet and outlet for the pulp, preferably with mixing means. For

example, a rotary glass reactor wherein mixing is achieved by rotation can be used. The gas injection can go on during a precalculated reaction time such as in a batch process. Otherwise, the contacting of the ozone with the pulp can be on a continuous basis with the pulp and ozone constantly being passed through the reactor. In such a continuous process, it must be assured that sufficient contact of the ozone with the pulp to destroy the catalase is achieved.

For example, at high consistency, the pulp that is contacted with the ozone is preferably dewatered and fluffed to permit the ozone easy access to the pulp fibers and allow a uniform reaction between the fibers and the ozone. For any type of pulp, the reaction time is usually very short and can vary greatly according to the reactor's configuration, sample size, ozone concentration, etc.

While the duration of the contact will vary depending on the foregoing, as well as other factors which are all well known to the skilled artisan, for the purposes of the present invention the "very short" contact generally will comprise at least 30 seconds, and more preferably at least one minute, up to about 6 minutes in duration. It must also be noted that the duration of the contact is associated with a smaller ozone charge as compared to an ozone charge which would be used to bleach the same amount of pulp.

The ozone gas is generally injected at almost atmospheric pressure. The amount of ozone used is generally in the range of from .01 to 0.15 wt. %, based on the weight of the dry pulp. More preferably, the amount of ozone used for the catalase deactivation or destruction is in the range of from about .05 to 0.15 wt. %, based upon the weight of the dry pulp.

When a liquid substance such as water is to be treated with ozone in order to inactivate or destroy catalase, the ozone generated can be bubbled through the water (or other solution). The amount of ozone used is generally in the range of from about .01 to about .15 wt. %, based upon the weight of water or liquid solution being treated, and more preferably in the range of from about .05 to about .15 wt. %. The contacting of the liquid solution can take place in accordance with conventional methods known to the art, e.g., in a closed container or in a container having a circulating atmosphere.

The contacting of catalase contaminated water with ozone can be of practical significance in a mill when attempting to avoid catalase contamination of uncontaminated pulp. The water used in the pulping process may very well be the source of contamination for the pulp. If desired, therefore, the water used in the mill can be so treated to avoid catalase contamination.

Once a pulp has been pretreated in accordance with the present invention, it can be subjected to a bleaching step using hydrogen peroxide with excellent results. The bleaching step can be run in accordance with any of the conventionally known processes for bleaching pulp. Generally, the conventional bleaching chemicals such as sodium hydroxide, silicates and DTPA are added together, optionally with water, in a container to adjust consistency. Hydrogen peroxide can then be added as the last chemical to the bleaching liquor. The pulp to be treated is generally contained in a suitable contained area, such as a conventional bleaching tower. The bleaching liquor is then added to the pulp, with mixing of the pulp in contact with the bleaching liquor then taking place.

In general, any conventional bleaching conditions can be used. As an example of such conditions, the hydrogen peroxide charge is generally in the range of from about 0.3 to 5 wt. %, based on the weight of oven dried pulp. If sodium hydroxide is used, the charge is generally in the range from about 0.3 to 3.0 wt. % based upon the weight of the oven dried pulp. If silicates are used, the charge is in the range of from about 2.0 to 3.0 wt. % based upon the weight of the oven dried pulp. If DTPA is used, the charge is generally in the range of from about 0.2 to 0.3 wt. % based upon the weight of the oven dried pulp. The temperature of the mixture of pulp and bleaching liquor is generally maintained in the range of from about 60 to 70 °C, with the bleaching reaction time ranging from about 60 to 180 minutes.

Once the bleaching reaction is completed, the pulp is removed from the bleaching tower. Handsheets from the pulp can then be made in order to check the final brightness. In general, the pretreatment with ozone has been found to result in a product having excellent, and even enhanced, brightness.

The use of ozone in the treatment of a substance or material contaminated with catalase in accordance with the present invention permits environmentally friendly, energy efficient destruction of the contaminating catalase. The present invention is particularly applicable to the pretreatment of pulp prior to a bleaching step with hydrogen peroxide. The pretreatment maximizes the bleaching step effect and therefore avoids the complications which generally occur when a catalase contaminated pulp is bleached with hydrogen peroxide. The ozone step has also been found to be able to slightly enhance the brightness of the pulp product beyond that which would normally be achieved if an uncontaminated pulp were bleached.

The invention will be illustrated in greater detail by the following specific examples. It is understood that these examples are given by way of illustration

and are not meant to limit the disclosure or the claims to follow. All percentages in the examples, and elsewhere in the specification, are by weight unless otherwise specified.

EXAMPLE 1

The following Example demonstrates how the presence of the enzyme catalase decomposes or causes the decomposition of hydrogen peroxide.

Hydrogen peroxide in a composition of about 9 grams per liter was added to a water solution containing catalase. The concentration of hydrogen peroxide was measured over time, with measurements being taken every few minutes. The results of the measurements are graphically depicted in Figure 1.

Several other samples of water contaminated with catalase were first treated with different amounts of ozone ranging from 0.3 to 0.025 grams of ozone per 200 milliliters of solution. Once treated, hydrogen peroxide was then added to the various samples at a concentration of about 9 grams per liter. The hydrogen peroxide concentration in the various treated water solutions were then measured over time. The results of these measurements are also depicted in Figure 1.

From the results, it can be seen that catalase decomposes hydrogen peroxide rapidly when not inactivated. As much as 80% decomposition of hydrogen peroxide can occur within 10 to 15 minutes.

This emphasizes the need to deal with the problem of catalase contamination of any pulp to be bleached using hydrogen peroxide.

When a catalase contaminated material, however, is treated with ozone, the catalase is inactivated. The result is that the hydrogen peroxide is not decomposed and the concentration of hydrogen peroxide is maintained as a constant. This is clearly shown by the results of the various samples which had been treated with ozone prior to the addition of hydrogen peroxide.

EXAMPLE 2

In this Example, a handsheet was made according to TAPPI methods using a thermo-mechanical pulp (TMP) in order to determine the brightness of the pulp. The brightness (% ISO brightness) was measured using El Reoho 2000 equipment. The brightness of the original mechanical pulp was about 79% ISO. The pulp was the divided into four equal samples, with each sample being treated differently as follows.

Sample 1 -

For the first sample, no catalase was added to the pulp and the pulp was subjected to a hydrogen peroxide bleaching treatment. The bleaching treatment involved the following procedure:

Preparation of the Sample -

The consistency of the sample was adjusted to about 10%. Next, the sample was preheated to about the desired reaction temperature using a water bath.

Bleaching Liquor -

The bleaching chemicals DTPA and sodium hydroxide, were added to a beaker. Hydrogen peroxide was then added to the bleaching liquor in an amount of 2% by weight of dry pulp, which is the same amount for each of the samples. The amount of DTPA used was about 0.2 wt. % based upon the weight of the pulp to be treated, and the amount of sodium hydroxide used was about 0.7 wt. % based upon the weight of the pulp to be treated.

Reaction -

The sample was placed in a plastic bag and the bleaching liquor was added to the pulp. The bag was sealed and mixing was carried out manually. The sealed bag was then placed in a preheated water bag at the reaction temperature of 70 °C for the reaction time of 60 minutes. After the reaction was completed, the bag was taken out of the water bath and liquor was squeezed from the sample to remove residual peroxide. A handsheet was also made in order to check the final brightness.

The final brightness of this first sample was measured to be about 83.5%. Residual peroxide was about 15% (based on the amount of H_2O_2 applied).

Sample 2 -

The second sample was treated with a water solution contaminated with catalase, and then subjected to the hydrogen peroxide bleaching procedure described above. The final brightness of the bleached pulp was determined to be 80.8% ISO. Residual peroxide was not found.

Sample 3 -

The third sample of pulp was treated with a catalase contaminated solution. Once treated with the catalase, the pulp was then contacted with

ozone.

The ozone was produced from oxygen in a 7 gram per hour ozone generator. The oxygen/ozone mixture prepared was then injected in a rotary glass reactor which contained the pulp. Mixing was achieved by rotation and the ozone was contacted with the pulp for one (1) minute. The amount of ozone employed in the closed system was about 0.1 wt. %, based upon the weight of the oven dried pulp.

The third sample (having been treated with the ozone) was then subjected to the peroxide bleaching procedure outlined above. The brightness of the third sample was determined to be 84.3% ISO. Residual peroxide was about 14%.

Sample 4 -

The fourth sample was treated with catalase contaminated water, and then boiled at 100 °C for 15 minutes. The boiled pulp was then subjected to the hydrogen peroxide bleaching procedure described above with respect to sample 1, with the brightness being measured. The brightness was measured as 84.1% ISO.

Residual peroxide was about 13%.

From the foregoing results, which are graphically depicted in Figure 2, it can be seen that a pretreatment with ozone effectively inactivates the enzyme catalase. As a result, a subsequent hydrogen peroxide bleaching procedure results in a pulp having enhanced brightness.

EXAMPLE 3

A furnish of 100% non-inked thermo-mechanical pulp (TMP) was used. This furnish was chosen based upon the fact that TMP can be bleached by hydrogen peroxide while ozone generally has little bleaching effect. In this way, we could concentrate on the effect the ozone had on the catalase enzyme.

30 gram pulp samples were contaminated with 0.02 grams of catalase (activity equals 18600 units/mg protein). One contaminated sample was directly treated with hydrogen peroxide in an amount of 1.5 wt. %. This amount was a larger charge than the 0.7 wt. % used in the remainder of the runs in order to effectively demonstrate the deleterious effect catalase has on the peroxide. Three other contaminated samples were first treated with small charges of ozone, i.e., .024 wt %, .05 wt.% and .15 wt. % ozone, and then bleached with a hydrogen peroxide charge of 0.7 wt. %. A non-contaminated sample was also treated with a 0.7 wt. % peroxide charge for comparison purposes. Sodium silicate and DTPA were added in all peroxide stages to prevent any peroxide decomposition by metal ions. The brightness of each bleached pulp was then measured.

Figure 3 graphically depicts the results of the various runs. It can be noted that an ozone charge of .024 and .05 wt. % did not completely deactivate the effect of the catalase applied, but did help improve the brightness of the pulp relative to the initial brightness. The 0.15 wt. % ozone treatment suggests total deactivation of the catalase, and in fact provides a slightly improved brightness as compared to a pulp which was not contaminated with catalase.

While the invention has been described with preferred embodiments, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and the scope of the claims appended hereto.

Claims

1. A process for bleaching pulp which comprises
   (i) contacting the pulp with from 0.01 to 0.15 wt % of ozone, based upon the weight of the dry pulp, for a period of time sufficient to destroy any catalase enzyme which may be contained in the pulp; and
   (ii) bleaching the ozone treated pulp with hydrogen peroxide.

2. A process according to Claim 1, wherein the pulp is a cellulosic pulp.

3. A process according to Claim 2, wherein the cellulosic pulp is a mechanical pulp or recycled pulp.

4. A process according to Claim 1, wherein the pulp is a cellulose free pulp.

5. A process according to any preceding claim, wherein the amount of ozone employed is in the contacting ranges from about 0.1 to 0.15 wt. %, based upon the weight of dry pulp being contacted.

6. A process according to one of Claims 1 to 5, wherein the amount of ozone used is in the contacting ranges from about 0.05 to about 0.15 wt. %.

7. A process according to Claim 4, wherein the cellulose free pulp is a recycled pulp.

8. A process for destroying the catalase content of a substance or material to be used in a pulp bleaching process which comprises contacting

a substance or material contaminated with catalase with ozone for a period of time sufficient to destroy the contaminating catalase enzyme, and with the amount of ozone being sufficient to destroy the catalase enzyme but insufficient to degrade or bleach the contaminated substance or material.

9. A process according to Claim 8, wherein the substance comprises water.

10. A process according to Claim 8 or 9, wherein the substance comprises a fibrous pulp.

11. A process according to Claims 8 to 10, wherein the substance comprises water and pulp.

12. A process according to one of Claims 8 to 11, wherein the amount of ozone used is in the contacting ranges from about 0.05 to about 0.15 wt. %, based upon the weight of the substance being contacted.

FIG. 1

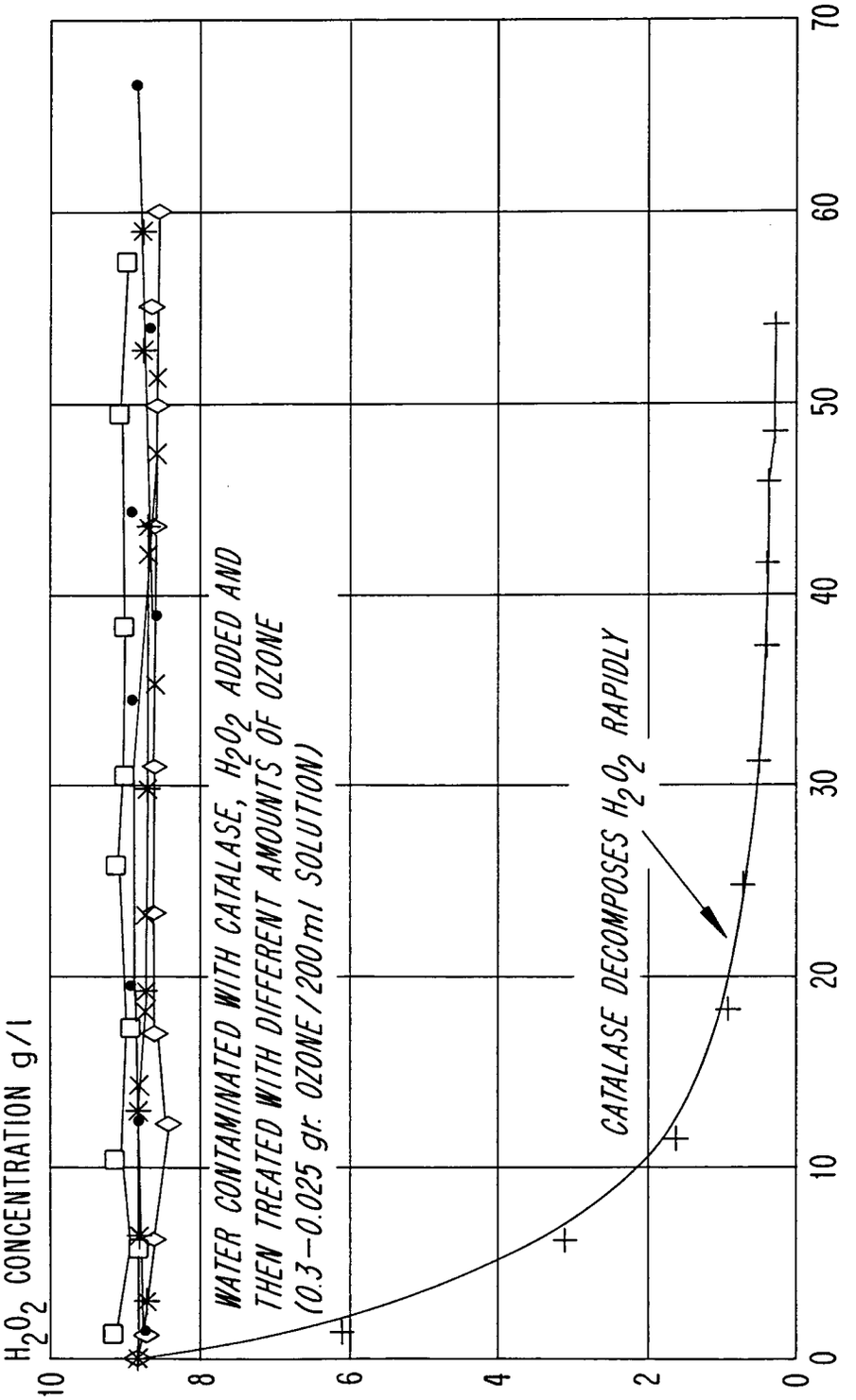

H_2O_2 CONCENTRATION g/l
10
8
6
4
2
0
0
10
20
30
40
50
60
70
TIME (MIN)
WATER CONTAMINATED WITH CATALASE, H_2O_2 ADDED AND THEN TREATED WITH DIFFERENT AMOUNTS OF OZONE (0.3–0.025 gr. OZONE/200ml SOLUTION)
CATALASE DECOMPOSES H_2O_2 RAPIDLY

FIG. 2

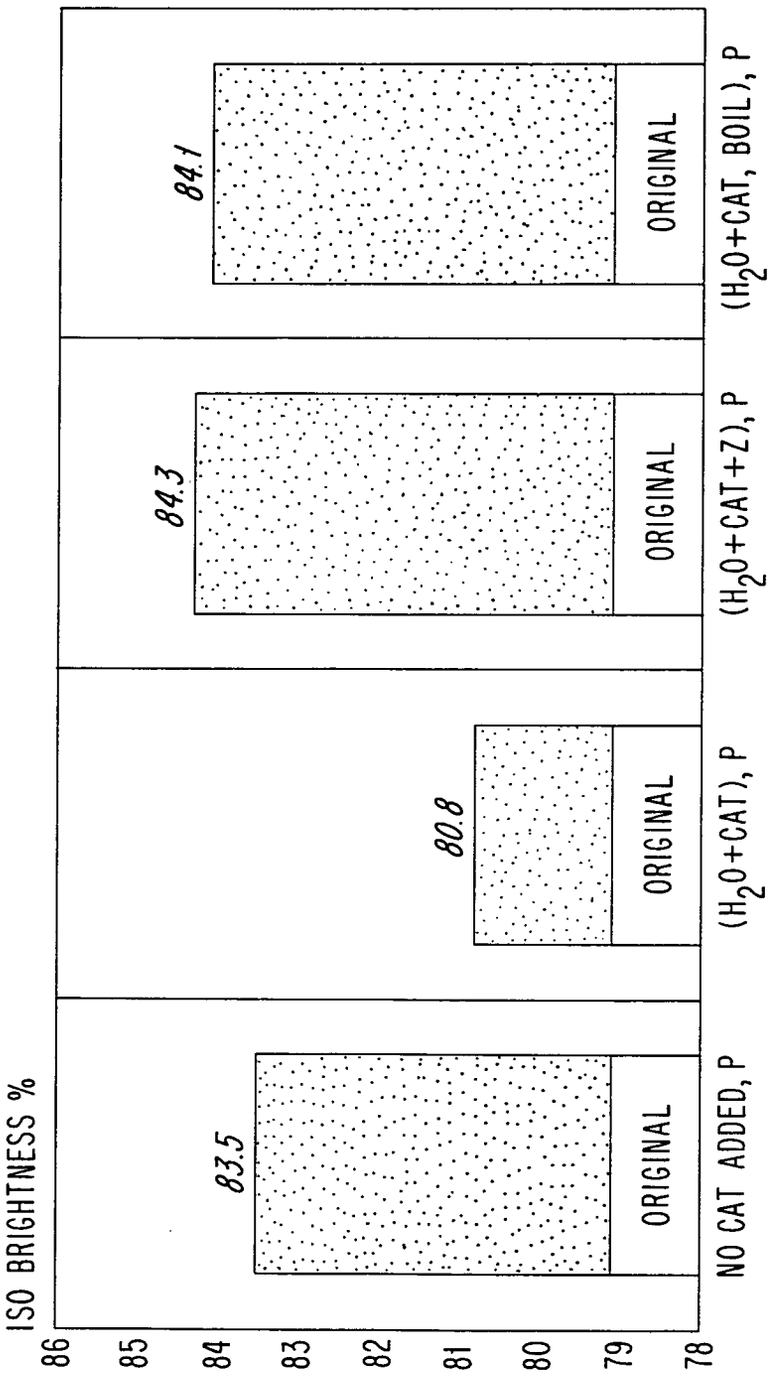
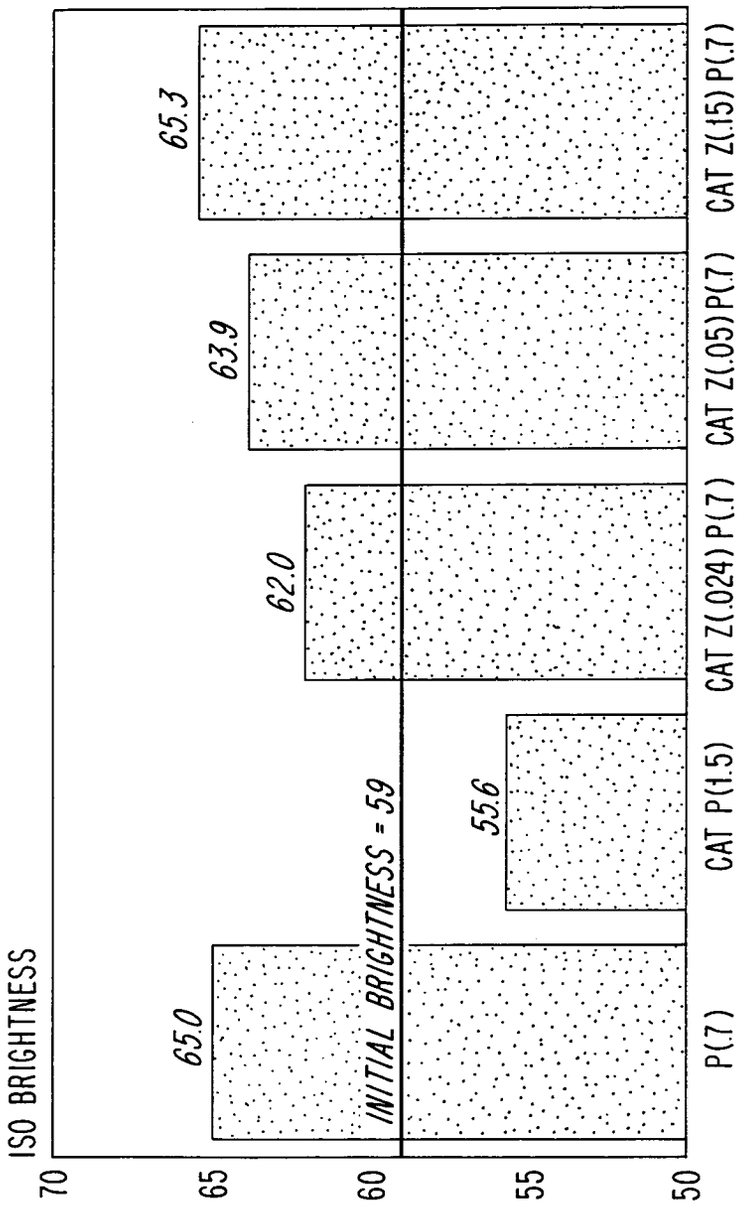

ISO BRIGHTNESS %
86
85
84
83
82
81
80
79
78
83.5
ORIGINAL
NO CAT ADDED, P
80.8
ORIGINAL
(H_2O+CAT), P
84.3
ORIGINAL
(H_2O+CAT+Z), P
84.1
ORIGINAL
(H_2O+CAT, BOIL), P

FIG. 3


ISO BRIGHTNESS
70
65
60
55
50
65.0
62.0
63.9
65.3
55.6
INITIAL BRIGHTNESS = 59
P(.7)
CAT P(1.5)
CAT Z(.024) P(.7)
CAT Z(.05) P(.7)
CAT Z(.15) P(.7)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 12 0739

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 562 835 (ALBRIGHT &WILSON LTD) * claims 1-24 * -----	1-12	D21C9/153 D21C9/16
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			D21C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 March 1995	Fouquier, J-P

CATEGORY OF CITED DOCUMENTS

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