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(54) PEROXIDE BLEACHING OF PULP

PEROXIDBLEICHEN VON ZELLSTOFF

BLANCHIMENT AUX PEROXYDES DE PATE A PAPIER

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DE-A- 3 617 942
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US-A- 3 951 732

- **TECHNICAL ASSOCIATION OF THE PULP AND PAPER INDUSTRY PROCEEDINGS, 1988, N. SOTELAND, "Use of MgO or CaO as the Only Alkaline Source in Peroxide Bleaching of High Yield Pulps", pages 231-236.**

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Description

FIELD OF THE INVENTION

[0001] THIS INVENTION relates to a process for peroxide bleaching of pulp. Pulps which may be bleached in the process of the invention include lignocellulose pulp which may be produced mechanically and chemi-mechanically with yields in the region of greater than 75% which are otherwise known as high yield pulps.

BACKGROUND OF THE INVENTION

[0002] In a conventional peroxide bleaching process, sodium hydroxide is used as an alkali source. To achieve a desired brightness with maximum efficiency, auxiliary substances are also used. Such auxiliary substances include sodium silicate, magnesium sulphate and chelating agents inclusive of DTPA (sodium salt of diethylene triamino pentaacetic acid).

[0003] Reference may be made to a prior art article by Soteland *et al.*, 1988, TAPPI Proceedings 231-236, which describes a peroxide bleaching process which utilises magnesium oxide as a sole alkaline source. The pulp was pretreated with DTPA and magnesium oxide particles were utilised in a size range of 1.00 mm - 0.25 mm or smaller. The magnesium oxide were also used in a concentration of 2-3% based on the dry weight of the pulp. The MgO used in the process was light-burnt MgO and finely crushed. It was found that brightness levels obtained were very close to that which was achieved by conventional bleaching using NaOH. In the bleaching process, the pulp was diluted to form a pulp suspension and the amount of MgO was added to the suspension under vigorous stirring. Hydrogen peroxide was subsequently added to the suspension at a concentration of 3% based on the weight of the pulp. This reference also made the observation that coarse particles are less effective as an alkaline source during peroxide bleaching.

[0004] Having regard to the abovementioned reference, an observation was also made in the corresponding patent specification DE-A-3617942 that use of MgO as sole alkaline source considerably simplified the bleaching process since sodium hydroxide as alkaline source and auxiliary chemicals such as sodium silicate could be omitted.

[0005] Another advantage of using MgO as sole alkaline source was that only a small amount of waste is produced in the bleaching plant. Thus, for example, in integrated mills which produce magnesium sulphite pulp and peroxide bleached high-yield pulps, the used bleaching liquor is combusted and the MgO may be recovered for re-use.

[0006] However, the use of MgO as sole alkaline source in a peroxide bleaching process has not as yet achieved widespread commercial acceptance because although the principle of utilising MgO as sole alkaline source was described in the Soteland *et al.* references, the means of reducing the principle to practice on a commercial scale has not yet been fully elucidated.

SUMMARY OF THE INVENTION

[0007] Surprisingly, it has now been discovered as disclosed in claim 1 that commercial usage of magnesium oxide as a sole alkaline source in peroxide bleaching of wood pulp may be achieved by employing MgO particles with a particle size of less than 500 micrometers, i.e. 5-500 micrometers and more preferably less than 75 micrometers and having particle surface area (PSA) of between 20-60 m^2/g and more preferably between 30-50 m^2/g. By using such parameters, an efficient peroxide bleaching process may be carried out most efficiently on a commercial scale which may be achieved within a maximum bleaching time of 180 minutes and achievement of a maximum target of ISO brightness of 65 in regard to freshly prepared pulp.

[0008] Utilizing MgO with parameters outside those stated above will result in a less efficient bleaching process leading to higher usage of chemicals and therefore higher operating costs.

[0009] The dosages of MgO that may be utilised in the process of the invention is 0.3-2% based on the weight of the pulp.

[0010] The amount of hydrogen peroxide that may be utilised in the process of the invention is from 1-5% based on the weight of the pulp.

[0011] To achieve maximum efficiency, the MgO particles are preferably added to the pulp in the form of a powder or slurry prepared *in situ.*

[0012] Preferably the MgO is added to the pulp simultaneously with the peroxide or prior to the addition of the peroxide.

[0013] Chelating agents also may be used in the process of the invention and such chelating agents may comprise DTPA, EDTA or HEDTA (hydroxy-ethylene diamine tetracetic acid). Preferably the chelating agent is added to the pulp simultaneously with addition of MgO particles, as well as prior to addition of MgO particles.

[0014] Bleaching times of 60-180 minutes may also be utilised by the process of the invention to achieve a target ISO brightness of 55-65.

BRIEF DESCRIPTION OF DRAWINGS

[0015] In several preferred embodiments concerning the process of the invention which are discussed hereinafter in relation to Experiments 1 and 2:-

> FIG. 1 is a graph showin the effect of particle size on CCS (Cold Caustic Soda) pulp and more specifically showing particle size vs brightness at different times;
> FIG. 2 refers to the results of Experiment 2 whereby various samples are plotted against final brightness;
> FIG. 3 also refers to the result of Experiment 2 and shows the effect of surface area on CCS pulp and more specifically showing particle size vs brightness at different times; and
> FIG. 4 shows the results of FIG. 3 when plotted against time.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

EXPERIMENT 1

EFFECT OF MGO PARTICLE SIZE ON THE BLEACHABILITY OF CCS PULP

Introduction

[0016] This work was performed to establish a relationship between MgO particle size and alkali performance in the bleaching of CCS (Cold Caustic Soda) wood pulp. Four grades of MgO were trialled, each one identified by its particle size distribution. Each sample of MgO had approximately the same surface area. Particle size and surface area for each of the samples is given in Table 1.

Summary of bleaching work

[0017] CCS (chemi-mechanical pulp), pre-treated with DTPA to remove metal ions, was retrieved from the washers in the bleach plant at the Boyer mill. An equivalent mass of 20 grams OD of pulp was weighed out and placed in a plastic breaker. DTPA was then added as 0.15% v/w on the pulp and mixed. MgO as 0.4% w/w, enough water to give a stock consistency of 12% and peroxide as 1.6% v/w on pulp was added and mixed for 2 minutes. The pulp was wrapped in plastic bags and placed into a constant temperature water bath at 65°C. A 3 gram OD sample was removed from the bath at intervals of 2, 3 and 4 hours. This was then made into a brightness hand sheet using the standard Boyer pulp mill method. These were dried overnight in a constant temperature/humidity room and tested for ISO brightness. This procedure was repeated for all MgO samples as well as with control pulp containing no MgO (sample J)

Results

[0018] The results of this study indicate that particle size is a key parameter for achieving efficient peroxide bleaching of chemic-mechanical pulp. The results shown in Table 2 and FIG. 1 of this study indicate that an MgO particle size of $< 75\ \mu m$ (samples G and F, d90 = 65 and 35 respectively) is required to achieve a target brightness for a given retention time of 2, 3 or 4 hours.

[0019] To achieve an equivalent brightness with samples C (d90 = 1500) or D (d90 = 3500), the chemical dosages of MgO and H_2O_2 would need to be increased.

EXPERIMENT 2

EFFECT OF MGO PARTICLE SURFACE AREA ON THE BLEACHABILITY OF CCS PULP

Introduction

[0020] This work was performed to establish a relationship between MgO particle surface area and alkali performance in the bleaching of CCS (Cold Caustic Soda) wood pulp. Five grades of MgO were trialled, each one identifiable by its particle surface area. Each sample of MgO had approximately the same particle size. Particle size and surface area data for each of the samples is given in Table 3.

Summary of bleaching work

[0021] CCS (chemi-mechanical) pulp, pre-treated with DTPA to remove metal ions, was retrieved from the washers in the bleach plant at the Boyer mill. For each sample, a mass of 10 g O.D. pulp was placed into a beaker and the approximate mass of chemicals added. The pulp was mixed for 2 minutes in a bench top mixer. The pulp was then wrapped in plastic bags and placed into a constant temperature water bath at 65°C. After two hours retention, the samples were removed from the bath and divided into two. Half the sample was returned to the bath for a further hour of reaction while the other half was made into 5 gram brightness hand sheets. These were dried overnight and then tested for ISO brightness. The work was repeated with samples taken at 2, 3 and 4 hours.

Results

[0022] In the previous study (Experiment 1), we determined that MgO particle size was important for peroxide bleaching efficiency. The results of this study indicate that particle surface area is also a key parameter for achieving maximum brightness for a given chemical dose. The results from these two independent studies (Tables 4 and 5, FIGS. 2 and 3) indicate that a surface area in the range 30-50 m^2/g (samples B and C) is required to achieve maximum brightness for a given retention time and chemical dose. Surprisingly, when the surface area is either decreased or increased, the peroxide bleaching efficiency is reduced as indicated in FIGS. 2 and 3 by the bell shaped curves with brightness plateaus between samples B and C. To achieve an equivalent brightness to samples B and C with samples A, D or E, the chemical charges of H_2O and MgO would need to be increased.

[0023] The results in FIG. 3, when plotted against time (FIG. 4), appear to indicate that a similar brightness will be achieved with four of the five samples when the bleaching time is extended indefinitely. However, indefinite bleaching time is not a commercial reality and there is a clear benefit, based on these results, in employing MgO particles with a specific size and surface area. In fact, if MgO particles, with parameters outside those stated in this document are used, then the target brightness may not be achieved without increasing chemical dose rates.

TABLES

[0024]

TABLE 1

Sample	Particle size d90 micrometer	Surface area m^2/g
F	35	38
G	65	35
H	1500	30
I	3500	30

TABLE 2

Sample	Surface Area m^2/g	Brightness		
		2 hr	3 hr	4 hr
F	< 40	61.39	62.17	62.88
G	< 75	61.22	61.94	62.69
H	< 2000	56.85	57.98	59.17
I	< 5000	56.32	56.19	56.97
J	0	54.3	55.03	55.04

TABLE 3

Sample	Particle size d90 micrometer	Surface area m^2/g
A	14	1

TABLE 3 (continued)

Sample	Particle size d90 micrometer	Surface area m^2/g
B	10	35
C	10	43
D	15 (d90 = 70)	98
E	11	142

TABLE 4

Sample	Surface Area m^2/g	Brightness	
		2 hr	3 hr
A	1	58.5	59.1
B	35	60.2	60.5
C	43	60.1	60.6
D	98	58.3	59.0
E	142	56.8	58.8

TABLE 5

Sample	Surface Area m^2/g	Brightness		
		2 hr	3 hr	4 hr
A	1	56.02	57.75	58.54
B	35	58.89	60.58	60.96
C	43	59.17	31.37	61.09
D	98	58.15	59.1	60.29
E	142	57.45	59.13	60.27

LEGENDS

TABLE 2

Bleaching conditions:

[0025]

MgO % w/w on oven dry pulp = 0.4%
H_2O_2 1.6%
DTPA = 0.15%
Temperature = 65°C
Initial brightness 47.1

TABLE 4

Bleaching conditions:

[0026]

MgO % w/w on oven dry pulp = 0.3%
H_2O_2 = 1.8%

DTPA = 0.1%
Temperature = 65°C
Initial brightness 43.5

TABLE 5

Bleaching conditions:

[0027]

MgO % w/w on oven dry pulp = 0.4%
H_2O_2 = 1.6%
DTPA = 0.15%
Temperature - 65°C
Initial brightness 47.1

FIG. 1

[0028] Effect of particle size on CCS pulp - Particle size vs brightness at different times.

FIG. 2

[0029] Sample number vs final final brightness.

FIG. 3

[0030] Effect of surface area on CCS pulp - Surface area vs brightness at different

FIG. 4

[0031] Effect of surface area on CCS pulp - Time vs brightness for different surface areas

Claims

1. A process for peroxide bleaching of pulp using magnesium oxide as sole alkaline source wherein said pulp is bleached in the presence of hydrogen peroxide for a maximum period of 180 minutes and achievement of a maximum target ISO brightness of 65 in regard to freshly prepared pulp characterised in that said magnesium oxide is utilised as MgO particles having a particle size of 5-500 micrometers and a particle surface area (PSA) of between 20-60 m^2/g.

2. A process as claimed in Claim 1 wherein said MgO particles have a particle size of less than 75 micrometers.

3. A process as claimed in Claim 1 wherein the MgO particles have a particle sizesurface area of between 30-50 m^2/g.

4. A process as claimed in Claim 1 which utilises a dosage of MgO which is 0.3-2% based on the weight of the pulp.

5. A process as claimed in Claim 1 wherein the amount of hydrogen peroxide utilised comprises 1-5 % based on the weight of the pulp.

6. A process as claimed in Claim 1 wherein the MgO particles are added to the pulp in the form of a powder or slurry prepared *in situ.*

7. A process as claimed in Claim 1 wherein the MgO particles are added to the pulp simultaneously with the addition of peroxide.

8. A process as claimed in Claim 1 wherein the MgO particles is added to the pulp prior to the addition of peroxide.

9. A process as claimed In Claim 1 wherein a chelating agent is added to the pulp selected from DTPA, EDTA or HEDTA.

10. A process as claimed in Claim 9 wherein the chelating agent is added to the pulp simultaneously with the addition of MgO particles.

11. A process as claimed In Claim 9 wherein the chelating agent is added to the pulp prior to the addition of MgO particles.

Patentansprüche

1. Verfahren zum Peroxidbleichen von Zellstoff unter Verwendung von Magnesiumoxid als einzige alkalische Quelle, dadurch gekennzeichnet, daß der Zellstoff in Anwesenheit von Wasserstoffperoxid maximal 180 Minuten lang gebleicht wird, und Erreichen eines maximalen ISO-Zielweißgrades von 65 in Bezug auf frisch hergestellten Zellstoff, dadurch gekennzeichnet daß das Magnesiumoxid in Form von MgO-Teilchen verwendet wird, die eine Teilchengröße von 5-500 Mikrometer und eine Teilchenoberfläche (PSA) von 20-60 m^2/g haben.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die MgO-Teilchen eine Teilchengröße von weniger als 75 Mikrometer haben.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die MgO-Teilchen eine Teilchenoberfläche von 30-50 m^2/g haben.

4. Verfahren nach Anspruch 1, bei dem eine MgO-Dosierung verwendet wird, die 0,3-2% auf der Grundlage des Zellstoffgewichts beträgt.

5. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Menge des verwendeten Wasserstoffperoxids 1-5% auf der Grundlage des Zellstoffgewichts aufweist.

6. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die MgO-Teilchen dem Zellstoff in Form von Pulver oder Schlamm, das bzw. der *in situ* hergestellt wird, beigegeben werden.

7. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die MgO-Teilchen dem Zellstoff gleichzeitig mit dem Peroxid beigegeben werden.

8. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die MgO-Teilchen dem Zellstoff vor dem Peroxid beigegeben werden.

9. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß dem Zellstoff als chelatbildendes Mittel DTPA, EDTA oder HEDTA beigegeben wird.

10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß das chelatbildende Mittel dem Zellstoff gleichzeitig mit den MgO-Teilchen beigegeben wird.

11. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß das chelatbildende Mittel dem Zellstoff vor den MgO-Teilchen beigegeben wird.

Revendications

1. Procédé de blanchiment au peroxyde d'une pâte à l'aide d'oxyde de magnésium en tant qu'unique source alcaline, dans lequel ladite pâte est blanchie en présence de peroxyde d'hydrogène pendant une durée maximale de 180 minutes, et l'obtention d'une blancheur ISO cible maximale de 65 par rapport à une pâte fraîchement préparée, caractérisé en ce que ledit oxyde de magnésium est utilisé sous forme de particules de MgO ayant une granulométrie de 5 à 500 micromètres et une surface spécifique de particule (PSA) comprise entre 20 et 60 m^2/g.

2. Procédé selon la revendication 1, dans lequel lesdites particules de MgO ont une granulométrie inférieure à 75 micromètres.

3. Procédé selon la revendication 1, dans lequel les particules de MgO ont une surface spécifique de particule comprise entre 30 et 50 m^2/g.

4. Procédé selon la revendication 1, qui utilise une dose de MgO qui est de 0,3 à 2 %, par rapport au poids de la pâte.

5. Procédé selon la revendication 1, dans lequel la proportion de peroxyde d'hydrogène utilisé constitue 1 à 5 % par rapport au poids de la pâte.

6. Procédé selon la revendication 1, dans lequel les particules de MgO sont ajoutées à la pâte sous forme d'une poudre ou d'une suspension préparée *in situ.*

7. Procédé selon la revendication 1, dans lequel les particules de MgO sont ajoutées à la pâte simultanément à l'addition du peroxyde.

8. Procédé selon la revendication 1, dans lequel les particules de MgO sont ajoutées à la pâte avant l'addition du peroxyde.

9. Procédé selon la revendication 1, dans lequel un agent chélatant est ajouté à la pâte choisi parmi le DTPA, l'EDTA ou l'HEDTA.

10. Procédé selon la revendication 9, dans lequel l'agent chélatant est ajouté à la pâte simultanément à l'addition des particules de MgO.

11. Procédé selon la revendication 9, dans lequel l'agent chélatant est ajouté à la pâte avant l'addition des particules de MgO.

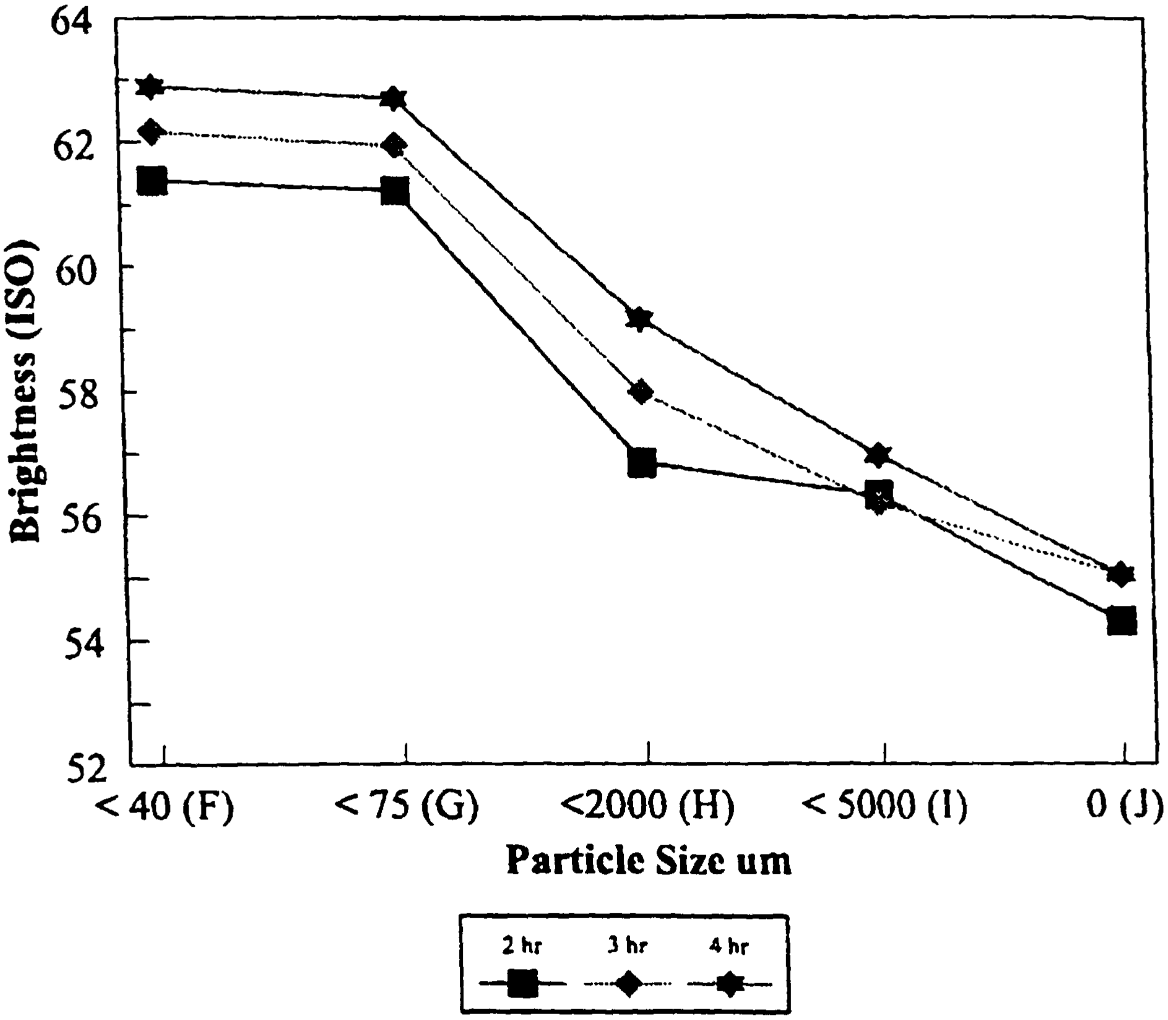
64
62
60
58
56
54
52
Brightness (ISO)
< 40 (F)
< 75 (G)
<2000 (H)
< 5000 (I)
0 (J)
Particle Size um
2 hr
3 hr
4 hr

FIG. 1

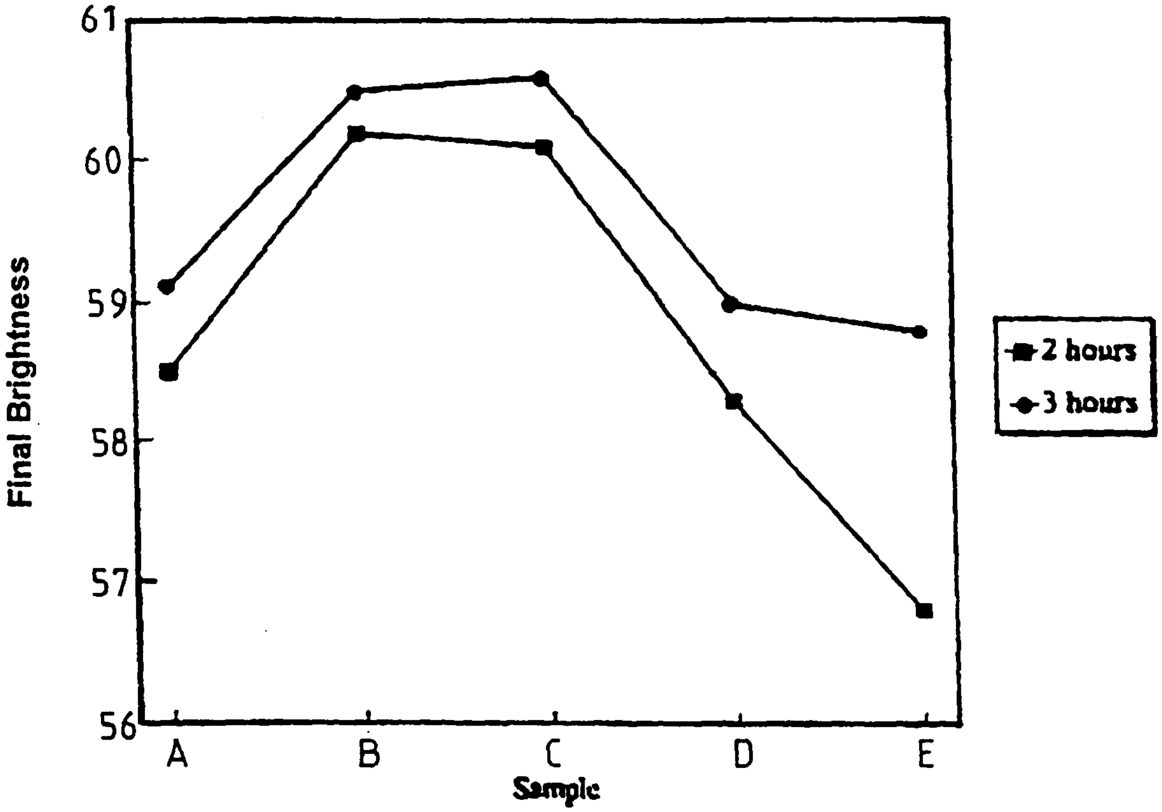
61
60
59
58
57
56
Final Brightness
A
B
C
D
E
Sample
■ 2 hours
● 3 hours

FIG. 2

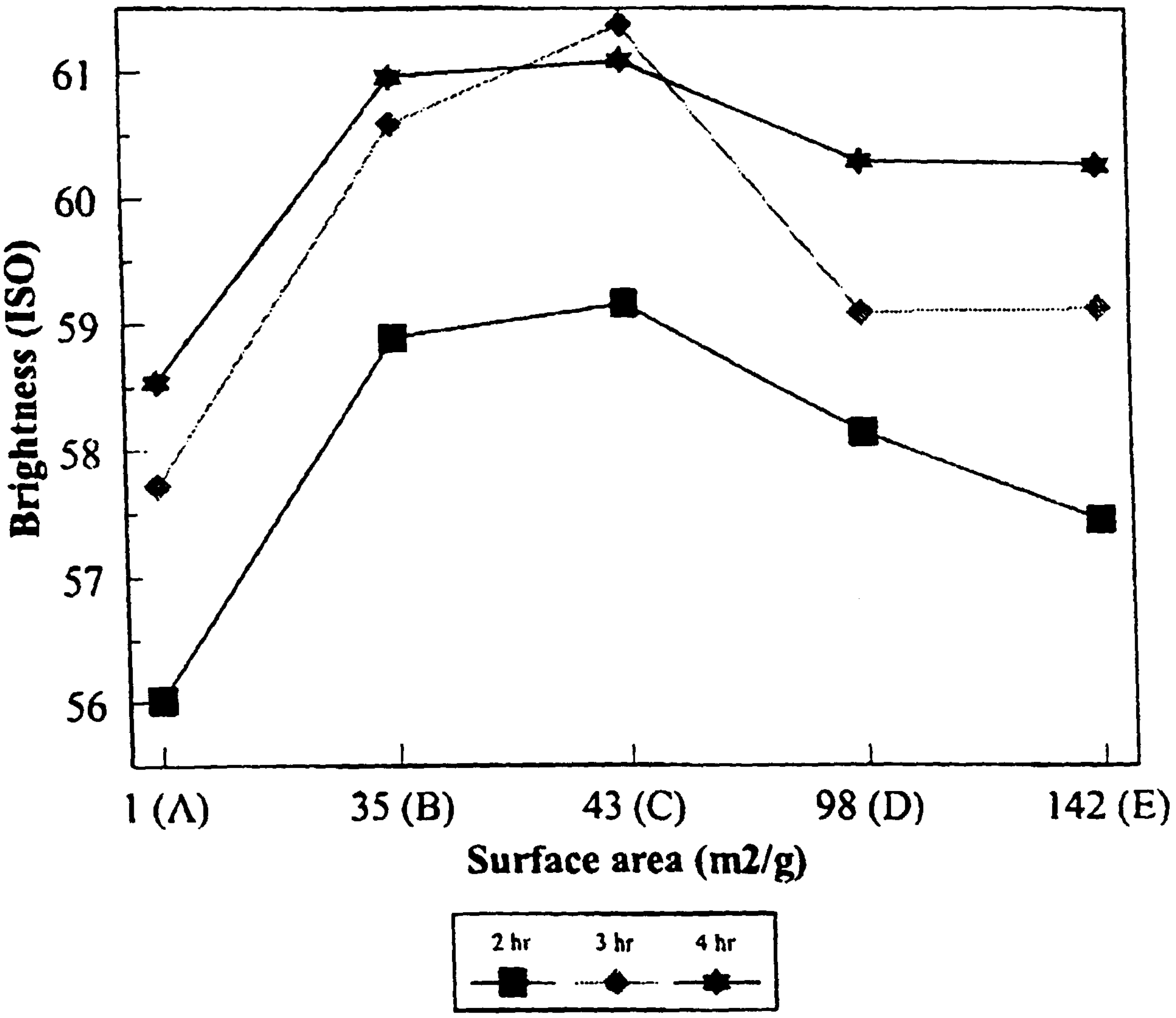
61
60
59
58
57
56
Brightness (ISO)
1 (A)
35 (B)
43 (C)
98 (D)
142 (E)
Surface area (m2/g)
2 hr
3 hr
4 hr

FIG. 3

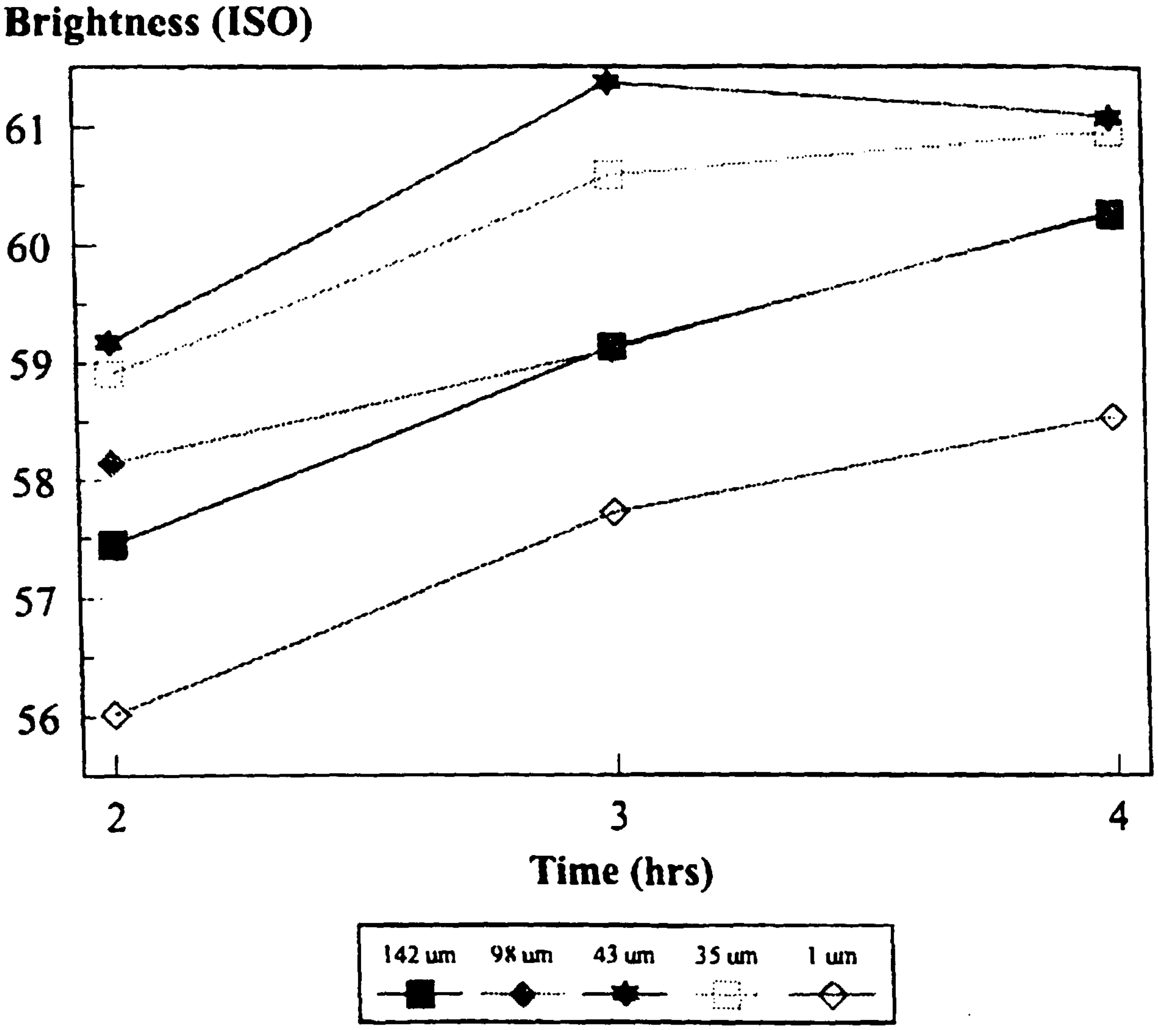
Brightness (ISO)
61
60
59
58
57
56
2
3
4
Time (hrs)
142 um
98 um
43 um
35 um
1 um

FIG. 4