



(12) UK Patent (19) GB (11) 2 062 661 B

(54) Title of invention

Product suitable for use as a textile finishing agent

(51) INT CL<sup>3</sup>: C08L 5/00

(21) Application No  
8035739

(22) Date of filing  
6 Nov 1980

(30) Priority data

(31) 92630  
193029  
193030

(32) 8 Nov 1979  
2 Oct 1980

(33) United States of America  
(US)

(43) Application published  
28 May 1981

(45) Patent published  
13 Jun 1984

(73) Proprietor  
Sun Chemical Corporation  
(USA-Delaware),  
200 Park Avenue  
New York  
New York  
United States of America

(72) Inventor  
Bernard Francis North

(74) Agent and/or  
Address for Service  
Marks & Clerk,  
57—60 Lincoln's Inn Fields  
London WC2A 3LS

(52) Domestic classification  
C3R 38B2B 38B3B 38B3C  
38D1B3 38D4A 38D4X 38E3D  
38N1C 38N1H 38N1M1  
38N1MX 38N1S 38N4 SM  
D1P 1212 1265 1300 1301  
1303 1317 1340 DL  
U1S 1597 3047 C3R D1P

(56) Documents cited  
JP 53—044567

(58) Field of search  
C3R

LONDON THE PATENT OFFICE

GB 2 062 661 B

1.

"PRODUCT SUITABLE FOR USE AS A TEXTILE FINISHING  
AGENT"

This invention relates to a product suitable for use as a textile finishing agent, and more particularly to a finishing resin that imparts crease-resistance to textile fabrics.

5           The use of thermosetting resins to impart crease resistance and dimensional stability to textile materials is well-known in the art. These materials, known as aminoplast resins, include the products of the reaction of formaldehyde with such compounds as urea, thiourea,  
10   ethylene urea, dihydroxyethylene urea, and melamines. A serious drawback to the use of such materials is that they contain free formaldehyde. This is present during the preparation and storage of the finishing agent and its use in treating textiles, on the treated fabric, and  
15   on the finished garments. Also, when the fabrics or garments made therefrom are stored under humid conditions, additional free formaldehyde is produced.

          The presence of even less than one per cent of free formaldehyde, based on the total weight of the  
20   product, is undesirable, not only because of its unpleasant odor, but because it is an allergen and an irritant, causing severe reactions in the operators who manufacture the agent and who treat and handle the treated fabrics and to persons who handle and wear garments  
25   fabricated from the treated fabrics.

These problems associated with the presence of free formaldehyde on treated fabrics are well-known and considerable efforts have been made to produce formaldehyde free textile fabrics. One solution to the problem has been to employ scavengers for the free formaldehyde. In U.S. patent No. 3,590,100 cyclic ethylene urea and propylene urea are disclosed as scavengers. Removal of the formaldehyde by reaction with phthalimide is disclosed in U.S. patent No. 3, 723,058. U.S. patent No. 4,127,382 teaches certain nitrogen-containing heterocyclic compounds as scavengers.

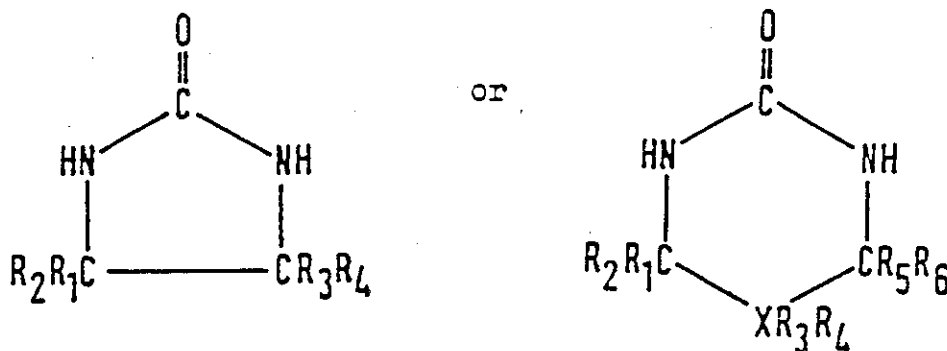
Treating textiles with resin compositions that do not contain or evolve formaldehyde is also known, as in U.S. patent No. 3,260,565 which teaches finishing agents formed by the reaction of alkyl or aryl ureas or thioureas with glyoxal. These agents, however, have the disadvantage of having marginal permanent press properties. Finishing agents formed by the reaction of ethylene urea with glyoxal are disclosed in Japanese patent publication No. 53-044567, but they too do not have satisfactory properties.

It has now been found that the alkylated products of the reaction of glyoxal and cyclic ureas are excellent cross-linking resins for textile fabrics and do not contain formaldehyde. Thus, in accordance with the present invention, novel alkylated glyoxal/cyclic urea condensates are prepared that are useful for crosslinking textile fabrics.

Accordingly, the present invention in one aspect provides an alkylated product of the reaction of glyoxal and at least one cyclic urea, wherein the ratio of the amounts of glyoxal:cyclic urea is 0.8:1 to 1.2:1.

5 The invention in another aspect provides a finishing agent for imparting crease-resistance to a textile, comprising an alkylated product according to the first aspect of the invention.

The cyclic ureas which may be used have the  
10 following general formulas :



wherein  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$ ,  $\text{R}_4$ ,  $\text{R}_5$  and  $\text{R}_6$  may be the same or different and each may be H, OH, COOH, R, OR or COOR wherein R is an alkyl or a substituted alkyl group  
15 having 1 to 4 carbon atoms, and X may be C, O, or N; wherein when X is O,  $\text{R}_3$  and  $\text{R}_4$  are each zero; and wherein when X is N,  $\text{R}_3$  or  $\text{R}_4$  is zero.

Typical examples of such compounds include ethylene urea, propylene urea, uron, tetrahydro-5-  
20 (2-hydroxyethyl)-1,3,5-triazin-2-one, 4,5-dihydroxy-2-imidazolidinone, and mixtures of these.

The invention in a further aspect provides a process for imparting crease-resistance to a textile, which comprises impregnating a textile with a solution of a finishing agent according to the invention and a catalyst, and heating the impregnated textile to cure the finishing agent thereon.

The alkylated condensates can be prepared by any suitable and convenient procedure. The cyclic urea and the glyoxal are preferably reacted in stoichiometric amounts, although a slight excess of either of the reactants may be employed. The range of glyoxal: cyclic urea is 0.8:1 to 1.2:1. The reaction may be carried out within the temperature range of room temperature up to reflux, but preferably is run at 50 to 60°C. for about two hours. The pH may suitably range from 2 to 7.0, and preferably it is within the range of 5.0 to 7.0. The product is a water-soluble oligomer. These glyoxal/cyclic urea condensates are then partially or wholly alkylated, e.g. by reacting them with an alcohol such as methanol, ethanol, n-propanol, a butanol, and their mixtures.

Another method involves reacting glyoxal with an alkylated cyclic urea.

The finishing agent of this invention is suitable for use with cellulosic textile fabrics, woven or non-woven, including 100% cellulosic fabrics, e.g. cotton,

rayon, and linen, as well as blends, e.g. polyester/  
cotton or polyester/rayon. Such blends preferably  
contain at least 20% of cellulose. Both white and  
coloured (printed, dyed, yarn-dyed, cross-dyed, etc.)  
5 fabrics can be effectively treated with the finishing  
agent of this invention, as can also fabrics containing  
fibers with free hydroxyl groups.

When applying the finishing agent of this invention  
to a fabric, there generally will be present an appropriate  
10 catalyst. Typical catalysts include acids (such as hydro-  
chloric, sulfuric, fluoboric, acetic, glycolic, maleic,  
lactic, citric, tartaric, and oxalic acids), metal salts  
(such as magnesium chloride, nitrate, fluoborate or  
fluosilicate, zinc chloride, nitrate, fluoborate or  
15 fluosilicate, ammonium chloride, zirconium oxychloride,  
sodium or potassium bisulfate), amine hydrochlorides (such  
as the hydrochloride of 2-amino-2-methyl-1-propanol), and  
mixtures thereof. The amount of catalyst generally is  
0.01 to 10 per cent, more preferably 0.05 to 5 per cent,  
20 based on the weight of the padding bath.

The finishing agents may be applied to the textile  
fabric in any known and convenient manner, e.g. by dipping  
or padding, and will generally be applied from aqueous  
or alcoholic solution. The solvent may be water, an  
25 aliphatic alcohol, e.g. methanol, ethanol, or isopropanol,  
or a mixture of water and an aliphatic alcohol. Other

conventional additives such as lubricants, softeners, bodying agents, water repellents, flame retardants, soil shedding agents, mildew inhibitors, anti-wet soiling agents, and fluorescent brighteners may be used in the treating bath in conventional amounts. Such auxiliaries must not, however, interfere with the proper functioning of the finishing agent, must not themselves have a deleterious effect on the fabric, and preferably be free of formaldehyde.

The amount of finishing agent which is applied to the fabric will depend upon the type of fabric and its intended application. In general the amount applied is 0.5 to 10 per cent, more preferably 2 to 5 per cent, based on the weight of the fabric.

In the process of treating fabrics with the finishing agents of this invention, the fabric is impregnated with an aqueous or alcoholic solution of the finishing agent, and the impregnated fabric is then dried and cured; the drying and curing steps may be consecutive or simultaneous.

If desired, the textile fabric may be finished by post-curing (also known as deferred or delayed curing). This consists of impregnating the fabric with a solution of finishing agent and catalyst, drying the impregnated material carefully so that the finishing agent does not react, and then, after a prolonged interval, heating the

material to a temperature at which the agent reacts under the influence of the catalyst.

Although this invention is described with reference to the use of the alkylated product of the reaction of a cyclic urea and glyoxal as a textile finishing agent it is not intended to be limited thereto. The product of the invention is also suitable for use for example as a dry-strength or a wet-strength resin in paper; a hand-builder in textiles; a binder in particleboard, medium-density fiberboard, plywood, foundry and shell molding, insulation materials including glass fiber mats, friction materials, coated and bonded abrasives, etc.; a component in molding compounds; an adhesive for wood and laminates; a film-forming resin in coatings and printing inks; an additive in fibers, e.g. rayon; an additive in rubber processing; an agent in leather tanning; a textile size; a dry fixative for textiles; and an impregnant for filters, e.g. automotive filters.

The invention will be further described with reference to the following illustrative Examples.



Unless otherwise specified, all parts and percentages are by weight.

EXAMPLE 1

290 Parts (2 moles) of a 40% aqueous solution  
5 of glyoxal was adjusted to pH 6.5 with sodium bicarbonate.  
176 Parts (2 moles) of ethylene urea was added and the  
temperature raised to  $55 \pm 5^\circ\text{C}$ . The mixture was stirred at  
this temperature for two hours, maintaining the pH between  
6.0 and 7.0. After two hours 200 parts (6.25 moles) of  
10 methanol was added and the pH adjusted to about 3.0 with  
concentrated sulfuric acid. The reaction was held at  
reflux for three hours to effect methylation, the resin  
solution cooled to  $30^\circ\text{C}$ ., and the pH adjusted to about  
7.0 with a 25% solution of caustic soda.

15 The product was a clear-viscous liquid, pale  
yellow, with negligible odor. The reaction was essentially  
complete, as determined by IR and NMR analyses. IR  
analysis indicated that methylation had occurred.

EXAMPLE 2

20 360 Parts (2.5 moles) of a 40% aqueous solution  
of glyoxal was added to 905 parts (2.5 moles) of a 44%  
methanol solution of dimethyl methoxy propylene urea.  
The mixture was heated to  $55 \pm 5^\circ\text{C}$ . for two hours, the pH  
being maintained between 6.0 and 7.0. After cooling at  
25  $30^\circ\text{C}$ . there was obtained a 45%-solids, slightly viscous,  
water-white solution with no odor of formaldehyde. The  
reaction was essentially complete, as determined by IR  
and NMR analyses.

EXAMPLE 3

30 The procedure of Example 1 was repeated except  
that the glyoxal was reacted with each of the following  
instead of ethylene urea: propylene urea, uron, tetra-  
hydro-5-(2-hydroxyethyl)-1,3,5-triazin-2-one, and 4,5-  
dihydroxy-2-imidazolidinone. The results were comparable.

EXAMPLE 4

The procedure of Example 1 was repeated except that each of the following alcohols was used instead of methanol: ethanol, n-propanol, and isopropanol. The results were comparable.

EXAMPLE 5

The resin product of Example 1 was used to treat 100% cotton fabric. The test results are tabulated below and compared with those of a sample of the same fabric treated with a conventional formaldehyde-containing agent. In each case the solution of resin and catalyst was applied to samples of the fabric by padding with a wet pickup of about 60%, based on the weight of the fabric. The treated fabrics were dried by heating for 3 minutes at 107°C., and the resin cured on the fabrics by heating for 90 seconds at 171°C.

Wrinkle Recovery was measured by AATCC Test Method 66-1978 "Wrinkle Recovery of Fabrics: Recovery Angle Method".

Tensile was measured by ASTM Test Method D-1682-64 (Reapproved 1975) "Tensile-Grab-CRT Pendulum Type".

TABLE I

	(a)	(b)	(c)
Reactant, parts			
A	15.0		
B		15.0	
Catalyst 531, parts	4.5	4.5	
Sulfanole® RWD, part	0.25	0.25	
Tensile			
warp	40	40	89
fill	16	15	37
Wrinkle Recovery			
initial	245	286	168
after 5 AHL	245	280	173

A is the product of Example 1.

B is 1,3-bishydroxymethyl-4,5-dihydroxy-2-imidazolidinone (45% aqueous solution).

(c) is untreated 100% cotton fabric.

5 Catalyst 531 (Sun Chemical Corporation) is an activated magnesium chloride catalyst.

Sulfanole<sup>®</sup> RWD (Sun Chemical Corporation) is a non-ionic wetting agent.

AHL is average home launderings.

10 From these data it can be seen that the fabric treated with the product of this invention (a) is comparable in tensile strength and wrinkle recovery to the fabric treated with a commercial formaldehyde-containing agent (b) and has the advantage of being free of formaldehyde.

15 EXAMPLE 6

The procedure of Example 5 was repeated with the resin products of Examples 2, 3, and 4. The results were comparable.

EXAMPLE 7

20 An aqueous solution containing 15.0 parts of the resin product of Example 1 and 4.0 parts of Catalyst 531 was applied to samples of 65/35 polyester/cotton fabric by padding. The treated fabrics were dried; the resin cured on the fabrics by heating for 5 minutes at 150°C.,  
25 5 minutes at 177°C., and 1 minute at 193°C.; and the fabric smoothness determined by AATCC Test Method 124-1978 "Appearance of Durable Press Fabrics after Repeated Home Launderings". The results are tabulated below.

TABLE II

		(a)	(d)
	Fabric Smoothness		
5	after 1 AHL		
	150°C.	3.7	3.2
	177°C.	3.6	3.1
	193°C.	3.4	3.0
	after 5 AHL		
10	150°C.	3.5	3.1
	177°C.	3.7	3.1
	193°C.	3.6	3.1
	after 10 AHL		
15	150°C.	3.4	3.2
	177°C.	3.8	3.2
	193°C.	3.8	3.2

(d) is untreated 65/35 polyester/cotton fabric.

The whiteness of the fabric (a) was good, and the fabric showed no chlorine scorch either initially or after 5 launderings.

20 EXAMPLE 8

The following solutions were prepared, applied to 100% cotton, and tensile and wrinkle recovery measured as in Example 5:

TABLE III

		(a)	(e)	(c)
25	Reactant, parts			
	A	15.0		
	C		15.0	
	Catalyst 531, parts	4.5	4.5	
30	Sulfanole® RWD, part	0.25	0.25	
	Tensile			
	warp	40	41	89
	fill	16	17	37
	Wrinkle Recovery			
35	initial	245	199	168
	after 5 AHL	245	187	173

A is the product of Example 1.

C is the product of the reaction of stoichiometric amounts of glyoxal and dimethyl urea (disclosed in U. S. patent No. 3,260,565).

5 (c) is untreated 100% cotton fabric.

From these data it can be seen that the fabric treated with the product of this invention (a) is comparable in tensile strength to the fabric treated with the reactant disclosed in U. S. patent No. 3,260,565 (e) and  
10 considerably superior to it in wrinkle recovery.

EXAMPLE 9

The procedure of Example 5 was repeated with each of the following fabrics instead of 100% cotton: 50/50 polyester/cotton, 65/35 polyester/cotton, 50/50  
15 polyester/rayon, and 65/35 polyester/rayon. The results were comparable.

EXAMPLE 10

A sample of 65/35 polyester/cotton fabric was impregnated with an aqueous solution containing 20 parts  
20 of the product of Example 1, 5 parts of Catalyst KR (Sun Chemical Corporation's magnesium chloride catalyst), and 0.25 part of Sulfanole RWD. The fabric was then dried at 100°C. and stored at elevated temperature for several weeks. A crease was then pressed into the fabric, and it  
25 was cured for 15 minutes at 150°C. The fabric was washed and evaluated by AATCC Test Method 88C-1975 "Appearance of Creases in Wash-and-Wear Items after Home Laundering". It had an appearance rating of 5 as compared with a blank having a rating of 3.

30 EXAMPLE 11

To illustrate the superiority of an alkylated glyoxal/cyclic urea condensate over a nonalkylated glyoxal/cyclic urea condensate, the following experiments were carried out:

35 (1) 176 Parts of ethylene urea (2 moles) was reacted with 320 parts of 40% glyoxal (2.2 moles) at a

pH of 6 and a temperature of 50-60°C. for two hours. The product was then reacted with 200 parts of methanol (6.25 moles) at pH 3.0, and then adjusted to pH 6.0 and 45% solids. The temperature was lowered to, and held at, 48°C., and viscosity measurements were taken at intervals with a Brookfield Viscometer.

(2) 176 Parts of ethylene urea (2 moles) was reacted with 320 parts of 40% glyoxal (2.2 moles) at a pH of 6 and a temperature of 50-60°C. for two hours. The product was adjusted with water to 45% solids. The temperature was lowered to, and held at, 48°C., and viscosity measurements were taken at intervals with a Brookfield Viscometer.

TABLE IV

Viscosity, cps	(1)	(2)
initial	52	26.5
after weeks - 1	65	gelled
- 2	107.5	
- 3	115	
- 4	127.5	
- 8	210	
- 9	232	
- 10	240	

(1) is an alkylated glyoxal/cyclic urea condensate.

(2) is a nonalkylated glyoxal/cyclic urea condensate.

From these data it can be seen that the non-alkylated product (2) was unstable, gelling in one week, whereas the alkylated product (1) remained stable after 10 weeks at 48°C.

#### EXAMPLE 12

To illustrate the superiority of an alkylated glyoxal/cyclic urea condensate over a nonalkylated glyoxal/cyclic urea condensate as a textile treating agent, the following experiments were carried out:

(1) Japanese publication No. 53- 044567 Example 1

300 Grams of ethylene urea was charged into a 4-necked flask equipped with a reflux condenser, a thermometer, and a stirrer and dissolved in 450 grams of water. Then 1 kg. of 40% glyoxal (glyoxal:ethylene urea ratio of 2:1) and 2 grams of concentrated hydrochloric acid were added. The mixture was reacted for three hours at 40°C. After cooling, the pH was adjusted to 5.0 with sodium hydroxide solution. The slightly coloured transparent product had a solids content of 40%.

(2) Japanese publication No. 53- 044567 Example 2

300 Grams of ethylene urea was charged into a flask as in (1) and dissolved in 450 grams of water. 750 Grams of 40% glyoxal (glyoxal:ethylene urea ratio of 1.5:1) and 2 grams of concentrated hydrochloric acid were added. The mixture was reacted for three hours at 40°C. After cooling, the pH was adjusted to 5.0 with sodium hydroxide solution. The slightly coloured transparent product had a solids content of 40%.

15 Parts of each of these products and of the product of Example 1 was each mixed with 3.75 parts of an activated magnesium chloride catalyst and 0.25 part of Sulfanole RWD, and the solutions were applied by padding to samples of fabric. The treated fabrics were dried for 3 minutes at 107°C. and the resin cured on the fabrics by heating for 90 seconds at 177°C.

The blue and whiteness indexes of each were measured by AATCC Test Method 110-1975 and are tabulated as follows:

30

TABLE V

	(a)	(f)	(g)	(h)
cotton				
blue index	81.85	74.83	76.16	85.46
whiteness index	65.53	42.04	47.69	78.23
35 65/35 polyester/cotton				
blue index	78.99	70.07	72.51	82.35
whiteness index	57.63	29.51	37.74	67.62

(a) is the product of Example 1 of this application.

(f) is the product of Example 1 of Japanese publication No. 53-044567.

5 (g) is the product of Example 2 of Japanese publication No. 53-044567.

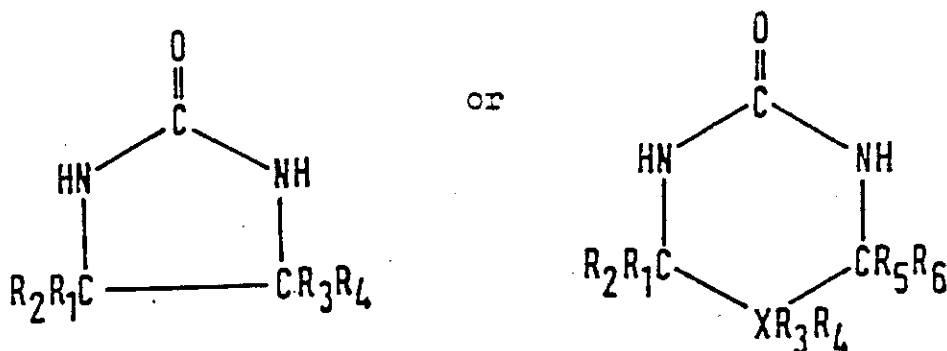
(h) is untreated fabric.

10 It is evident from these data that the product of this invention (a) is superior to the products of the Japanese publication (f) and (g) in both blue index and whiteness index. In addition, it was noted that the dry scorch on the fabrics treated with products (f) and (g) was extremely severe.



C L A I M S :

1. An alkylated product of the reaction of glyoxal and at least one cyclic urea, wherein the ratio of the amounts of glyoxal: cyclic urea is 0.8:1 to 1.2:1.
2. A product as claimed in Claim 1, wherein the  
5 cyclic urea has the formula :



wherein  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$  and  $R_6$  may be the same or different and each may be H, OH, COOH, R, OR or COOR wherein R is an alkyl or a substituted alkyl group  
10 having 1 to 4 carbon atoms, and X may be C, O, or N; wherein when X is O,  $R_3$  and  $R_4$  are each zero; and wherein when X is N,  $R_3$  or  $R_4$  is zero.

3. A product as claimed in Claim 2, wherein the cyclic urea is ethylene urea, propylene urea, uron,  
15 tetrahydro-5-(2-hydroxyethyl)-1,3,5-triazin-2-one, 4,5-dihydroxy-2-imidazolidinone, or a mixture thereof.
4. An alkylated product according to Claim 1, as described in any of the foregoing Examples 1 to 4.

5. A finishing agent for imparting crease-resistance to a textile, comprising an alkylated product as claimed in any of Claims 1 to 4.

6. A process for imparting crease-resistance to a  
5 textile, which comprises impregnating a textile with a solution of a finishing agent as claimed in Claim 5 and a catalyst, and heating the impregnated textile to cure the finishing agent thereon.

7. A process according to Claim 6, substantially  
10 as herein described in any of the foregoing Examples 5 to 12.

8. A crease-resistant textile produced by the process as claimed in Claim 6 or 7.

9. A water-soluble resinous product prepared by  
15 alkylating the product of the condensation of glyoxal and at least one cyclic urea, the ratio of glyoxal: cyclic urea being 0.8:1 to 1.2:1.

10. A resinous product prepared by condensing  
glyoxal with at least one alkylated cyclic urea,  
20 the ratio of glyoxal:cyclic urea being 0.8:1 to 1.2:1.

The text of the specification has been reproduced by photocopying the applicants original typescript. It may contain a few amendments which are difficult to read. The original typescript containing these amendments may be inspected on the premises of the Patent Office

2062661

2062661

Dated: 6 November 1980

Application No.: 8035739

Published: 28 May 1981

Priority:

8 November 1979  
2 October 1980  
2 October 1980

United States of America 92630  
United States of America 193 029  
United States of America 193 030

SUN CHEMICAL CORPORATION, 200 Park Avenue, New York, New York, United States of America,  
a Corporation organized and existing under the Laws of the State of Delaware, United  
States of America

BERNARD FRANCIS NORTH, 624, Plainfield Road, Rock Hill, South Carolina, United States of  
America,

Product suitable for use as a textile finishing agent:

Address for Service:

Marks ( ) Clerk, 57/60 Lincolns Inn Fields, London WC2A 3LS

Request for examination: **29 MAY 1981**

Application refused

Or withdrawn:

Patent granted:

WITH EFFECT FROM **15 JUN 1984**  
SECTION 25(1)

Renewal Fee paid in respect of

5th Year	
6th Year	
7th Year	
8th Year	
9th Year	
10th Year	
11th Year	
12th Year	
13th Year	
14th Year	
15th Year	
16th Year	
17th Year	
18th Year	
19th Year	
20th Year	

Patent ceased or

expired:



**THE PATENT OFFICE**  
25 Southampton Buildings London WC2A 1AY  
Telegrams Patoff London WC2  
Telephone 01-405 8721 ext 3363

RENEWAL DETAILS

PATENT No .....2062661.....

RENEWAL DATE .....6/11/80.....

*first renewal fee due*  
RENEWAL FEE PAID FOR ..... YEAR ON 6 Nov 1984

NOTE :

*[Signature]*  
.....  
FOR THE CONTROLLER

RENEWALS FILED WITHIN THE LAST FEW DAYS MAY NOT  
APPEAR IN THE RECORDS