OPTICAL BRIGHTENERS OF THE STILBENE SERIES
Heinrich Hausermann, Riehen, Switzerland, assignor to J. R. Geigy A.G., Basel, Switzerland
No Drawing. Filed Dec. 18, 1964, Ser. No. 419,566
8 Claims. (Cl. 260-507)

ABSTRACT OF THE DISCLOSURE
Optical brightening agents are provided in the free acid form are of the formula:

\[
R_1 - CO \left[ \begin{array}{c} \text{HN} \\ \text{CO} \end{array} \right]_a \text{HN} \text{CH} = \text{CH} \text{NH} \left[ \begin{array}{c} \text{CO} \\ \text{NH} \end{array} \right]_b \text{CO} - R_2
\]

wherein \( R_1 \), \( R_2 \) and \( X \) are as defined in the specification. Such agents are useful in the optical brightening of organic textile fibers containing hydroxyl groups, especially cellulosic fibers. The invention also provides organic fibers optically brightened by utilizing the new optical brighteners of the invention.

The present invention concerns new optical brighteners of the stilbene series, processes for the production thereof, detergents and brightening liquids containing these brighteners as active ingredients, a method for the optical brightening of organic textile fibers containing hydroxyl groups, especially cellulosic fibers, with the aid of the new brighteners, as well as industrial products, the aforementioned organic fibers optically brightened by a content of the new optical brighteners of the stilbene series.

It is known that optical brighteners of the class of N-substituted 4,4'-diaminostilbene-2,2'-disulphonic acids have only slight fastness to chlorine so that they can be used with compounds giving off chlorine in washing agents and liquids only at considerable expense to the optical effect.

It is however, increasingly desired by industry to have available detergents and wash liquids which permit at the same time, in a single treatment e.g. laundering, chemical bleaching and brightening white textile materials. At the same time, it is required that the brightening agents impart a neutral white shade, with a bluish, or possibly a very light violet hue, which appears very faintly pinkish to the naked eye, but not a greenish hue, to the brightened textile materials.

Known brightening agents which possess satisfactory fastness to chlorine and could therefore be used in detergents and the like media, containing chlorine-yielding compounds, have an undesirable tendency to impart an increasingly greenish shade to the treated materials, especially after repeated washing with liquids containing such known brighteners.

Moreover, since preferred liquid detergents and laundering baths nowadays contain non-ionogenic rather than ionogenic detergent constituents, it is necessary that a brightening agent, to be fully satisfactory, also draw sufficiently from a laundering bath containing the same onto cellulosic and the like textile materials, preferably with the chlorine-yielding bleaching agent present in the bath.

Known brightening agents which possess satisfactory chlorine-fastness, and would also impart neutral white shades to the treated cellulosic materials, fail because their affinity to cellulose fibers is so low that they do not draw efficiently onto these fibers from a bath containing essentially non-ionogenic detergent agent under normal laundering and bleaching conditions.

The present invention remedies these drawbacks of the known brighteners by providing brightening agents which, in the free acid form, are of the formula

\[
R_1 - CO \left[ \begin{array}{c} \text{HN} \\ \text{CO} \end{array} \right]_a \text{HN} \text{CH} = \text{CH} \text{NH} \left[ \begin{array}{c} \text{CO} \\ \text{NH} \end{array} \right]_b \text{CO} - R_2
\]

in which formulæ \( R_1 \) and \( R_2 \) each represent an unsubstituted or non-chromogenically substituted hydrocarbon radical as defined below,

\( X \) represents alkyl of from 1 to 5 carbon atoms, and preferably methyl or ethyl; lower alkoxy-lower alkyl, e.g., ethoxy-ethyl or propyloxy-propyl; alkyl or alkyl ether of from 1 to 2 carbon atoms substituted by phenyl, chlorophenyl, bromophenyl, lower alkylphenyl or lower alkoxyphenyl; or di-lower alkyl-aminopropylidene, piperidino, morpholino, lower alkyl-morpholino, and hexamethylene imino,

\( n \) and \( m \) represent 0 or 1, which brighteners, for the first time, combine:

(a) Satisfactory resistance to chlorine, so that they can be used in detergents and laundering liquids together with chlorine-yielding bleaching agents,

(b) A neutral white shade imparted to the treated textile cellulosic materials, and

(c) Good affinity to cellulosic fibers when drawing thereon from liquids containing non-ionogenic compounds as the essential detergent constituents.

By "non-chromogenic substituents" are meant substituent groups which do not impart color to the brightener molecule.

Each of \( R_1 \) and \( R_2 \) represent different or, preferably, identical radicals selected from the group consisting of

\( (\text{lower alkyl})_2 \),

\( (\text{lower alkyl})_3 \),

\( R_2'(\text{lower alkyl})_2 \),

\( R_2'(\text{alkoxy})_2 \),

wherein the alkyl moiety has from 2 to 4 carbon atoms,
In aqueous solutions of adettent containing brighteners according to the invention which are used for the brightening of the fiber mentioned, the content of brightener is preferably 0.005 to 0.5% by weight calculated on the weight of the detergent mixture. Suitable detergents contain as wash-active substances, e.g. anionic compounds, e.g. alkali metal salts, particularly sodium salts of higher fatty acids, alkali metal alkyl-aryl-sulfonates, especially dodecylbenzene sulfonate or tetrapropylbenzene sulfonate, or alkali metal secondary alkyl sulfates having at least one higher molecular secondary alkyl radical, fatty alcohol sulfates such as dodecyl sulfate or sulfated fatty alcohol polyglycol ethers such as sulfated addition products of 2 to 3 mols of ethylene oxide to dodecyl alcohol. The new brighteners draw easily and evenly onto cellulose material even in the presence of non-ionogenic wash-active substances, e.g. of polyglycol ethers containing lipophilic radicals. Examples of such non-ionogenic was-active compounds are fatty alcohol polyglycol ethers or alkylphenol polyglycol ethers. In addition, the detergents can contain the additives usual in the textile finishing industry such as water-soluble phosphates, silicates, carbonates, sulfates such as sodium sulfate water softeners, foam stabilizers and/or textile softeners.

Because of their excellent fastness to chlorine, the stilbene compounds according to the invention can be used without undue loss of brightening effect in detergents containing chlorine-yielding bleaching agents.

Such bleaching agents are, for instance, open or cyclic compounds containing the group —N—Cl such as N,N'-dichloroisocyanuric acid, chlorohydantoins or N-chloroaryl sulfonic acid amides such as N-chloro-p-toluene sulfonic acid amide or N-chloroalkyl sulfonic acid amides as well as such alkali metal or alkaline earth metal hypochlorites which are stable in solid state, e.g. lithium or calcium hypochlorite, these agents can be contained in the detergents and washing liquors, whereas hypochlorites which are instable in a solid state such as sodium or potassium hypochlorite can be used in the washing liquors.

The brightening agents according to the invention draw well from an aqueous solution of the type described above onto organic fibers containing hydroxyl groups, such as cellulose, particularly cotton, and lend to this material a pleasing pure white, bluish fluorescent appearance. Advantageously the brightened fibers have a content of 0.001 to 0.5% of brightening agent, calculated on the weight of the fibers.

Brighteners according to the invention are produced by a process which is illustrated by the diagram below. The new brightening agent of Formula I are advantageously isolated from the reaction mixture in the form of their alkali metal salts.
The 4,4'-diamino-6,6'-(di-alkyl-sulfonfyl)-stilbene-3,3'-disulfonic acids of Formula V are obtained by reducing 2-methyl-4-chlorobenzene-1-sulfonic acid chloride with sodium sulfite to form 2-methyl-4-chlorobenzene-1-sulfonic acid, reacting the latter by alkylation or the like, e.g. with dialkyl sulfate to form the corresponding 1-alkyl-sulfonfyl)-2-methyl-4-chloro-benzene; nitrating this substance with a mixture of nitric acid/sulfuric acid to form 1-alkylsulfonfyl-2-methyl-4-chloro-5-nitrobenzene (Formula II) and reacting this intermediate with aqueous sodium sulfite to form a 2-nitro-4-alkyl-sulfonfyl-5-methylbenzene-1-sulfonic acid of Formula III; oxidizing the sodium salt thereof with aqueous sodium hypochlorite to form the corresponding 4,4'-dinitro-6,6'-di-alkyl-sulfonfyl-stilbene-3,3'-disulfonic acid and reducing the nitro groups to amino groups.

While starting materials of Formula II in which X represents alkyl, are obtained from 1-alkysulfonfyl - 2-methyl-4-chloro-benzene by nitration as mentioned above, starting materials in which X represents lower alkoxy-alkyl are obtained in an analogous manner, alkoxy-alkylating the above mentioned sulfonic acid in lieu of alkylation the same.

Starting materials of Formula II in which X represents a dialkylamino radical are obtained from 2-methyl-4-chloro-benzene-1-sulfonic acid by nitrination to 2-methyl-4-chloro-5-nitro-benzene-1-sulfonic acid, chlorination with chlorosulfonic acid to 1-chlorosulfonfyl-2-methyl-4-chloro-5-nitro-benzene, and reaction of the latter with dialkylamine.

Starting materials in which X represents an unsubstituted or substituted benzyl or phenylethyl radical are obtained by reducing the above mentioned 1-chlorosulfonfyl-2-methyl-4-chloro-5-nitro-benzene with sodium sulfite to the corresponding sulfinic acid and simultaneously or successively exchanging the chlorine atom in 4-position by the —SO$_2$H group, consuming a second mol of sodium sulfite, and reacting this intermediate with an unsubstituted or substituted benzyl or phenylethylchloride.

By using for acylation of the intermediate of Formula V mixtures of compounds of the formulas $R_1$—COCI and $R_2$—COCI there are obtained final mixed brightener products with different substituents $R_3$ and $R_2$ in ratios which depend largely on the ratio in which the aforesaid chlorides have been added. These mixtures are used as brightening agents without separation of the individual compounds therefrom, since such separation into individual components would be without any commercial interest.

Intermediate materials of Formula VI in which $m$ and/or $n=1$ are obtained from the intermediate 4,4'-diaminostilbene-3,3'-disulfonic acids VII by reaction with p-nitrobenzene carboxylic acid halides and reduction of the nitro groups to amino groups.

Reactive derivatives of organic carboxylic acids of the formula $R_1$—COOH or $R_2$—COOH mainly anhydrides, chlorides or bromides of these acids, (sometimes also ketenes), and also organic half esters of carboxylic acid of the formula $R_1$—O—COOH or $R_2$—O—COOH in the latter case mainly the chloroformic or bromoformic acid esters of lower alkanols, are used as acylating agents. In the acylation steps of the above diagram, chlorides and bromides of aromatic carboxylic acids, in particular benzoic acid chlorides or bromides the ring of which is
3,394,173

substituted by lower alkoxy groups and/or lower alkyl groups particularly in one of the ortho- and/or the para-
position, are preferred. Examples of such aromatic car-
boxylic acid chlorides and bromides are 4-methoxy-
or 4-ethoxy-benzoyl chloride or bromide, 3-methyl-4-methoxy-
or 2,4-dimethoxy-benzoyl chloride or bromide, 2-methoxy-
4-methyl- or 2-ethoxy-4-methyl-benzoil chloride or bro-
clide, 2-methoxy-4-ethyl- or 2-ethoxy-4-ethyl-benzoil chloride or bromide, 2-methoxy-4,5-dimethyl-or 2-ethoxy-
4,5-dimethyl-benzoil chloride or bromide, or 3,4,5-tri-
methoxy-benzoil chloride or bromide.

The dianisimostibene compounds of Formula V or
VII are advantageously acylated in the present of tertiary
organic nitrogen bases, optionally in the presence of inert
organic solvents and, preferably, in the absence of water,
at a temperature of about 20–120°C, in particular be-
tween 80 and 100°C. Suitable tertiary nitrogen bases are,
mainly, pyridine and its homologues, tri- lower alkyl-
amines, triethylendiamine and di-lower alkyl anilines; ex-
amples of inert organic solvents are optionally halogenated
or nitritated aromatic hydrocarbons.

The following examples illustrate the invention. Where
not otherwise stated, parts and percentages are given by
weight. The temperatures are in degrees centigrade. The
relationship of parts to weight to parts by volume is as
that of kilograms to liters. Where not otherwise stated,
solutions are aqueous.

**EXAMPLE 1**

![Chemical Structure]

40 parts of 4,4'-diamino-6,6'-dimethylylsulfonyl-stilbene-
3,3'-disulfonic acid (Intermediate (a)) are suspended in
400 parts by volume of anhydrous pyridine and a solu-
tion of 40 parts of 2-ethoxy-4-methylbenzoyl chloride in
50 parts of anhydrous toluene is added dropwise and the
mixture is heated for 2 hours at 100–110°C. At the end of
this time, another solution of 40 parts of 2-ethoxy-4-methylbenzoyl chloride in 50 parts of an-
hydrous toluene is added dropwise and the mixture is
heated for another 2 hours at 100–110°C. By the end of
this time, no more free aromatic amino groups can be traced. The dark colored reaction solution
is then allowed to cool.

The reaction product separates out as a yellowish mass
which becomes solid when cold. The crude product is
purified by first washing with benzene, drying for a short
time, suspending it in 1200 parts by volume of 5% sodium
carbonate solution, heating the suspension at 70–80°C
while stirring, again cooling, filtering off the yellowish
product of the above formula, washing with 2.5 sodium
chloride solution and drying at 80°C in vacuo. In this way,
a pale yellow water-soluble powder is obtained the di-
luted aqueous solution of which has a blue fluorescence
in daylight. If uncolored cellulose fibers are treated with
aqueous solutions of the product, then a beautiful, neutral
white effect is obtained on the strata mentioned. The
product is available to agents giving off chlor-
line which enables both optical and chemical bleaching
to be performed in one bath. Another advantage of the
product is that it has the property to draw onto cellulose
fibers also in the presence of non-ionogenic washing
agents.

The 4,4'-diamino - 6,6'- dimethylylsulfonyl-stilbene-3,3'-
disulfonic acid of the formula

\[ \text{Formula} \]

used in the above example is obtained in the following
manner:

120 parts of sodium sulfite are dissolved in 480 parts
of water. To this solution there are added at a tempera-
ture of 65 to 70°C within 20 minutes, while stirring well.
142 parts of 2-methyl-4-chlorobenzene-1-sulfonic acid
chloride and a solution of 47 parts of sodium hydroxide in
110 parts of water. The addition of the sodium hydroxide
solution has to be performed at such a rate, that the pH
value of the mixture remains at 8 to 9.

After an additional stirring for 30 minutes at the same
temperature and pH, the reaction solution is clarified
and the sodium salt of the 2-methyl-4-chlorobenzene-1-
sulfonic acid is salted out with 15% of solid sodium chlo-
ride (calculated on the total weight of the reaction mix-
ture). 106 parts of the sodium salt of the aforesaid sul-
fonic acid precipitate upon cooling in a form of white,
easily water-soluble crystals which are separated by fil-
tration. The free sulfonic acid is obtained from a concen-
trated aqueous solution of the sodium salt by addition of
an excess of hydrochloric acid, and has a melting point of
91. The 106 parts of the sodium salt of the above mentioned
sulfonic acid are dispersed in 130 parts of water and heated
up to 70–75°C. At this temperature, 160 parts of dimethyl
sulfate are added within 45 minutes while the pH value of
the mixture is adjusted to 8 to 8.5 by simultaneous
addition of a sufficient amount of aqueous sodium hy-
droxide solution. After the addition of dimethyl sulfate,
the reaction mixture is stirred at the same temperature
and pH for an additional hour. After cooling to 10°C, the
reaction product is filtered off with suction and washed
with water. 2-methyl-4-chlorobenzene-1-methyl sulfone,
which is thus obtained in a yield of about 80%, forms
colorless crystals and melts at 70°C.

51.1 parts of 2-methyl-4-chlorobenzene-1-methyl sul-
fone are dissolved at 25°C in 250 parts of concentrated sul-
fonic acid. To this solution there are added dropwise at
a temperature of 1°C to 10°C within 1 to 2 hours, while stir-
ing well, a mixture consisting of 17 parts of nitric acid
(100% HNO₃) and 17 parts of concentrated sulfuric acid.
The whole batch is then stirred at 0°C to 10°C for a further 3
hours. In order to isolate the formed nitro compound,
the reaction mixture is poured on to 600 parts of crushed
ice, the nearly white precipitate is filtered off and washed
well with water. The product is dried at 75°C under re-
duced pressure to yield 62 parts (99% of the theoretical
amount) of crude 2-methyl-4-chloro-5-nitrobenzene-1-
methyl sulfone. This product melts at 127–130°C. The pure
product (M.P. 137°C) is obtained in a yield of about 85%
by recrystallization from ethanol. 10 parts of ethanol for
every part of crude 2-methyl-4-chloro-5-nitrobenzene-1-
methyl sulfone being required.

50 parts of 2-methyl-4-chloro-5-nitrobenzene-1-methyl
sulfone are dispersed in a mixture of 60 parts of ethanol
and 140 parts of water. To the well stirred mixture there
is added at 80 to 82°C within about 30 minutes a freshly
prepared solution of 25.2 parts of sodium sulfite in 100
parts of water. During the addition of the sulfite solution,
the pH is maintained in the range of 7.5 to 9 by addition
of a few drops of diluted hydrochloric acid. To complete
the reaction, the mixture is stirred at the same tempera-
ture for an additional 10 minutes. Thereafter, 32 parts
of solid sodium chloride are added and the reaction mixture
is cooled down to 10°C. A thick slurry is formed which is
filtered off by suction and the obtained crude product is
purified in the following manner: The wet filter cake is
dissolved in 250 parts of hot water, cooled down to 25
8,394,173 to 35°, clarified by filtration, the filtrate is then salted out at 60 to 70° with 55 parts of solid sodium chloride and cooled to 10°. Thereby, the sodium salt of the 2-nitro-4-methylsulfonyl-5-methylbenzene-1-sulfonic acid is obtained in nearly colorless crystals. The product is filtered off and dried at 80° under reduced pressure. This intermediate is obtained in a yield of 75%.

52.5 parts of the sodium salt of 2-nitro-4-methylsulfonyl-5-methylbenzene-1-sulfonic acid are dissolved in 900 parts of water. After raising the temperature to 30°, a solution of 28 parts of sodium hydroxide in 65 parts of water is poured in, then a solution of sodium hypochlorite and sodium hydroxide, prepared from 100 parts by volume of a sodium hypochlorite solution containing 17 parts of active chlorine and 4 parts of sodium hydroxide, is added dropwise within 25 to 30 minutes. A slightly exo-

thermic reaction takes place and the temperature remains without external heating at 30 to 35°. The di-sodium salt of 4,4'-dinitro-6,6'-dimethylsulfonyl-stilbene-3,3'-disulfonic acid separates in glittering, yellow needles from the dark brown solution. After the addition of the above sodium hypochlorite solution, the reaction mixture is stirred for 1 hour at 35°. The separation of the new stilbene derivative is completed by the addition of 25 parts sodium chloride, the whole is cooled down to 15 to 20°, the product filtered off, washed with aqueous 5% sodium chloride solution and dried at 80° under vacuum. The yield is 32.5 parts of di-sodium salt, corresponding to 30.2 parts of the free acid (62% of the theoretical amount).

20 parts of cast iron powder are suspended in 500 parts of water, 2 parts of acetic acid are added and the whole is heated for 30 minutes at 80 to 90° while stirring well. 19.2 parts of the di-sodium salt of 4,4'-dinitro-6,6'-dimethylsulfonyl-stilbene-3,3'-disulfonic acid are added to the iron suspension at 90 to 95° within a time of 20 minutes. The reaction mixture is then stirred for 1 hour at the boil. Thereafter, an aqueous solution of 2.4 parts of sodium carbonate is added and the iron residue is filtered off hot and washed with hot water until the filtrate gives no more diazo reaction. The yellowish solution is acidified with 15 parts by volume of 30%-hydrochloric acid, whereby 4,4'-diamino-6,6'-dimethylsulfonyl-stilbene-3,3'-disulfonic acid separates as a slightly cream colored precipitate. This intermediate product is filtered off, washed with water and dried at 80° under reduced pressure.

Products having a similar effect are obtained by replacing the 40 parts of 4,4'-diamino-6,6'-dimethylsulfonyl-stilbene-3,3'-disulfonic acid by an equivolam amount of one of the 4,4'-diamino-stilbene-3,3'-disulfonic acids [intermediates (a) to (s)] which bear in 6- and 6'-position the following substituents:

(b) amylsulfonyl
(c) β-methoxy-ethyl-sulfonyl
(d) α-methoxy-ethyl-sulfonyl
(e) γ-methoxy-propyl-sulfonyl
(f) β-methoxy-propyl-sulfonyl
(g) benzyl sulfonyl
(h) β-phenyl-ethyl-sulfonyl
(i) 3,4-dichloro-benzyl-sulfonyl
(j) 4-methoxy-benzyl-sulfonyl
(k) 2,4-dimethyl-benzyl-sulfonyl
(l) 4-methoxy-benzyl-sulfonyl
(m) dimethylamino-sulfonyl
(n) diethylamino-sulfonyl
(o) pyrroldino-sulfonyl
(p) piperidino-sulfonyl
(q) morpholino-sulfonyl
(r) 2,6-dimethylmorpholino-sulfonyl
(s) hexamethylene-imino-sulfonyl

and following otherwise the procedure given in the example. The intermediate products (e) to (l) inclusive are produced in the same manner as described in Example 1 for intermediate (a) using the corresponding 2-methyl-4-chlorophenyl-5-nitro-1-alkylsulfoes as starting materials.

The intermediates (m) to (s) inclusive are produced as described in Example 61, infra, for the case of 4,4'-diamino-6,6'-dimethylamino-sulfonyl-stilbene-3,3'-disulfonic acid.

Example 2

25.2 parts of 4,4'-diamino-6,6'-dimethylsulfonyl-stilbene-3,3'-disulfonic acid in 2000 parts by volume of anhydrous toluene are heated to 65-70° and, at this temperature while stirring, first 100 parts by volume of anhydrous pyridine and then, within 15 minutes, a solution of 60 parts of 2,4-dimethoxybenzoyl chloride in 300 parts of anhydrous toluene are added. The yellowish suspension obtained is stirred for 1 hour at 100-110°. At the end of this time, another portion of 25 parts of 2,4-dimethoxybenzoyl chloride in 75 parts by volume of anhydrous toluene is added and the whole is stirred for 2 hours at 100-110°. After cooling, the yellowish precipitate is filtered off, the product is suspended in 2000 parts by volume of water and, at 50-60° while stirring, 15% sodium carbonate solution is added until the pH of the mixture remains at 8.5-9. Any toluene and pyridine remaining is removed with steam, the aqueous suspension is cooled to 20° and the pale yellowish reaction product of the above formula which separates out is filtered off. After washing with 2.5% sodium chloride solution, the product is dried at 80° in vacuo. A pale yellow powder is obtained, the dilute aqueous solution of which has a blue fluorescence in daylight.

This product can be used for the brightening of cellulose fibers. Cotton fabric can be chemically and optically bleached in one step by the combined use of brightener and sodium hypochlorite. Also, in a non-ionicogenic washing liquor with and without bleachers giving off chlorine, the product gives beautiful, neutral white effects.

Example 3

14.5 parts of dry disodium salt of 4,4'-diamino-6,6'-dimethylsulfonyl-stilbene-3,3'-disulfonic acid are suspended in 125 parts by volume of abs. pyridine, 10 parts of 2-methoxy-4,5-dimethoxybenzoyl chloride are added to the mixture and the whole is heated for 2 hours at 110° while stirring. At the end of this time another 10 parts of 2-methoxy-4,5-dimethoxybenzoyl chloride are added and the whole is stirred for another 2 hours at 110°. To work up the product, 50 parts by volume of water are added to the reaction mixture at 80 to 90°, the reaction is made alkaline with 30% sodium hydroxide solution while stirring until phenolphthalein paper is clearly red, the pyridine is removed with steam and, after cooling, the yellowish reaction product of the above formula is filtered off and washed with 3% sodium chloride solution. After drying, a yellowish powder is obtained which has a bluish fluorescence in cold water. Like the products of the previous examples, it can be used for the brightening of cellulose.
substrata. This compound too is distinguished by very good stability to aqueous alkali hypochlorite solution. By replacing the 10 parts of 2-methoxy-4,5-dimethylbenzoyl chloride in Example 3 by equimolar amounts of the acid chlorides given in the second column of the following Table 1 and using Table 1 and 14.5 parts of the 4,4-diaminostilbene 3,3'-disulfonic acid employed in said example or replacing the same by an equimolar amount of one of the intermediates (b) to (s) inclusive obtained as described after Example 1, while otherwise following the procedure given in the said example, corresponding end products are obtained which are almost colorless to slightly yellowish powders of similar brightening properties as the products of Examples 1 to 3.

Table 1

<table>
<thead>
<tr>
<th>Acid chloride</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>21 (a-s)</td>
<td>Butyl chloroformate.</td>
</tr>
<tr>
<td>22 (a-s)</td>
<td>Ethyl chloroformate.</td>
</tr>
<tr>
<td>23 (a-s)</td>
<td>Methyl chloroformate.</td>
</tr>
<tr>
<td>24 (a-s)</td>
<td>3,4-dimethyl-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>25 (a-s)</td>
<td>3,4-dichloro-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>26 (a-s)</td>
<td>3,4-dimethyl-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>27 (a-s)</td>
<td>3,4-dichloro-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>28 (a-s)</td>
<td>3,4-dimethyl-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>29 (a-s)</td>
<td>3,4-dichloro-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>30 (a-s)</td>
<td>3,4-dimethyl-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>31 (a-s)</td>
<td>3,4-dichloro-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>32 (a-s)</td>
<td>3,4-dimethyl-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>33 (a-s)</td>
<td>3,4-dichloro-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>34 (a-s)</td>
<td>3,4-dimethyl-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>35 (a-s)</td>
<td>3,4-dichloro-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>36 (a-s)</td>
<td>3,4-dimethyl-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>37 (a-s)</td>
<td>3,4-dichloro-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>38 (a-s)</td>
<td>3,4-dimethyl-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>39 (a-s)</td>
<td>3,4-dichloro-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>40 (a-s)</td>
<td>3,4-dimethyl-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>41 (a-s)</td>
<td>3,4-dichloro-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>42 (a-s)</td>
<td>3,4-dimethyl-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>43 (a-s)</td>
<td>3,4-dichloro-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>44 (a-s)</td>
<td>3,4-dimethyl-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>45 (a-s)</td>
<td>3,4-dichloro-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>46 (a-s)</td>
<td>3,4-dimethyl-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>47 (a-s)</td>
<td>3,4-dichloro-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>48 (a-s)</td>
<td>3,4-dimethyl-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>49 (a-s)</td>
<td>3,4-dimethyl-thiophene-2-carboxylic chloroformate.</td>
</tr>
<tr>
<td>50 (a-s)</td>
<td>3,4-dichloro-thiophene-2-carboxylic chloroformate.</td>
</tr>
</tbody>
</table>

M.26 parts of 4,4'-diamino-6,6'-dimethylsulphonyl-stilbene-3,3'-disulfonic acid are suspended in 50 parts by volume of anhydrous pyridine and, after the addition of 6.5 parts of 2-acetoxycarbonylmethylbenzoyl chloride, the whole is heated for 1 hour at 100-110°. First 300 parts by volume of water and then, at 85-90°, 15% sodium carbonate solution are added to the brownish reaction mixture obtained, the latter addition being made dropwise, until the pH of the mixture has risen to 9-9.5 and, on discontinuation of the addition of alkali, does not sink below 9. The pyridine is then removed with steam and the intermediate product of the formula

\[
\text{CH}_2\text{CONH} - \text{CH}_2\text{OH} - \text{SO}_2\text{Na} \quad \text{SO}_2\text{Cl}_2
\]

which is formed is precipitated as a yellow precipitate by the addition of sodium chloride. 8.39 parts of this intermediate product are dissolved in 200 parts by volume of water and 0.8 parts of sodium hydroxide and 1.6 parts of ethylene chlorohydrin are added dropwise while stirring at 60-70°. When the reaction mixture no longer has an alkaline reaction, concentrated aqueous sodium hydroxide solution is added until the pH has risen to at least 12. Then ethylene chlorohydrin is added dropwise until the mixture has become neutral. The alternate addition of sodium hydroxide and ethylene chlorohydrin is repeated until a sample of the reaction mixture no longer shows a brown-violet colour with ferric chloride solution. After cooling, the pale yellow reaction product of the above formula is filtered off, washed with 4% sodium chloride solution and dried at 90°. A yellowish, water soluble powder is obtained which also has good substantivity in spite of its good water solubility and it can be used as brightener for cellulose fibers.

Products having a similar action are obtained by using 6.5 parts of 2-acetoxycarbonylmethylbenzoyl chloride or an equivalent amount of the acid chloride given in the second column of the following Table II, and also using

5.26 parts of 4,4'-diamino-6,6'-dimethylsulfonyl-stilbene-3,3'-disulfonic acid employed in said Example 51 or replacing the latter acid by an equimolar amount of or of the intermediates (b) to (s) inclusive given after Example 1, and as stated in the third column of Table II by directly saponifying the resulting product, in the man-
ner described in Example 51, or by replacing in the Example 51, the ethylene chlorohydrin by an equimolar amount of the bromides listed in the third column of the following Table II.

<table>
<thead>
<tr>
<th>Example No.:</th>
<th>Acid Chloride</th>
<th>Bromide</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 (a-a)</td>
<td>2-acetoxy-ethyl chloroformate</td>
<td>Do.</td>
</tr>
<tr>
<td>32 (a-a)</td>
<td>2-acetoxy-propionyl chloride</td>
<td>Do.</td>
</tr>
<tr>
<td>33 (a-a)</td>
<td>4-acetoxy-phenyl-acetyl chloride</td>
<td>Saponification.</td>
</tr>
<tr>
<td>34 (a-a)</td>
<td>4-acetoxy-phenyl-acetyl chloride</td>
<td>Ethylene bromohydrin.</td>
</tr>
<tr>
<td>35 (a-a)</td>
<td>4-acetoxy-ethyl chloroformate</td>
<td>Saponification.</td>
</tr>
<tr>
<td>36 (a-a)</td>
<td>4-acetoxy-benzyl chloroformate</td>
<td>Ethylene bromohydrin.</td>
</tr>
<tr>
<td>37 (a-a)</td>
<td>2-bis(acetoxy)benzoyl chloride</td>
<td>Do.</td>
</tr>
<tr>
<td>38 (a-a)</td>
<td>2-bis(acetoxy)benzoyl chloride</td>
<td>Do.</td>
</tr>
</tbody>
</table>

**TABLE II**

**EXAMPLE 61**

\[
\begin{align*}
\text{CHO} & \quad \text{CONH} & \quad \text{SO}_2\text{NH}(\text{CH}_3) \quad \text{SO}_2\text{NH}(\text{CH}_3) \\
\text{CH} &= \text{CH} & \quad \text{CONH} & \quad \text{SO}_2\text{NH}(\text{CH}_3) \quad \text{SO}_2\text{NH}(\text{CH}_3) \\
\text{OCH}_3 & \quad \text{SO}_3\text{H} & \quad \text{H} & \quad \text{SO}_3\text{H}
\end{align*}
\]

When in Example 2 the 52.6 parts of 4,4'-diamino-6,6'-diethylmethylsulfonyl-stilbene-3,3'-disulfonic acid are replaced by 58.8 parts of 4,4'-diamino-6,6'-bis-dimethylamino-stilbene-sulfonic acid, the d-sodium salt of the above mentioned acid is obtained which has, in spite of its good solubility in water, similar brightening properties as the corresponding di-methylsulfonyl compound. This product is isolated from its aqueous solution by salting out with 15% of solid sodium chloride (calculated on the total weight of the solution). The purified product forms a slightly yellowish powder, the aqueous solution of which exhibits in daylight a pronounced bluish fluorescence.

The 4,4'-diamino-6,6'-bis-diethylamino-stilbene-3,3'-disulfonic acid in the above example is obtained in the following manner:

94.5 parts of the sodium salt of 2-methyl-4-chloro-5-nitro-benzene-1-sulfonic acid are added while stirring well to 480 parts of chlorosulfonic acid at 15 to 20°C.

**EXAMPLE 62**

\[
\begin{align*}
\text{CHO} & \quad \text{CONH} & \quad \text{SO}_2\text{NH}(\text{CH}_3) \quad \text{SO}_2\text{NH}(\text{CH}_3) \\
\text{CH} &= \text{CH} & \quad \text{CONH} & \quad \text{SO}_2\text{NH}(\text{CH}_3) \quad \text{SO}_2\text{NH}(\text{CH}_3) \\
\text{OCH}_3 & \quad \text{SO}_3\text{H} & \quad \text{H} & \quad \text{SO}_3\text{H}
\end{align*}
\]

The whole mixture is subsequently stirred at 75°C for a further two hours. In order to isolate the formed 2-methyl-4-chloro-5-nitro-benzene-1-sulfonic acid chloride, the solution is poured onto 1400 parts of crushed ice, the grayish precipitate is filtered off, washed well with water and dried at 60°C in vacuum. The sulfochloride melts at 114–116°C and crystallizes from acetone in nearly white needles.

A solution of 82 parts of this sulfochloride in 400 parts of acetone is poured, while stirring, onto 600 parts of crushed ice. To this suspension of 2-methyl-4-chloro-5-nitro-benzene-1-sulfonic chloride is added a solution of 35 parts of dimethylamine in 50 parts of water. During the addition the temperature is kept down to 4 to 2°C. The yellowish slurry is then filtered off and the 2-methyl-4-chloro-5-nitro-benzene-1-sulfodimethylamide washed with water. The new product melts at 128°C.

To obtain the sodium salt of 2-nitro-4-dimethylsulfamido-5-methylbenzene-1-sulfonic acid the 2-methyl-4-chloro-5-nitro-benzene-1-sulfodimethylamide is reacted with sodium sulfite in a mixture of ethanol and water, in the manner as described in Example 1 for the production of the di-sodium salt of the corresponding methylsulfonyl compound. This product forms only faintly coloured, water soluble crystals.

35 parts of sodium hydroxide and 0.1 part of sodium laurate are dissolved in 100 parts of water, after the addition of a solution of 0.1 part of manganese sulfate in 20 parts of water, there are added at a temperature of 33° to 34° 24 parts of the above described sodium salt in 500 parts of water within 10 hours while blowing into the reaction mixture a strong stream of oxygen. The reaction solution is then clarified and the well water soluble 4,4'-dinitro - 6,6'-bis-dimethylsulfamido-stilbene-disulfonic acid in form of its brownish disodium salt salted out by saturation with sodium chloride.

The reduction of this dinitro-compound into the required diamino-product is carried out in the same manner as described in Example 1 for the production of the corresponding dimethylsulfonyl compound.

Products of similar good properties are obtained by replacing Example 61, but replacing in the same the acylating agent (used in Example 51) by one of the acylating agents used in Examples 1 to 50 inclusive, and/or by replacing in Example 61 the 35 parts of dimethylamine by an equimolar amount of one of the amines listed in Table III below, whereby intermediates (n) to (z) inclusive listed following Example 1 and others are obtained.

**TABLE III**

| (a) diethyamine |
| (b) pyrrolidine |
| (c) piperidine |
| (d) morpholine |
| (e) 2,6-dimethyl morpholine |
| (f) hexamethylene imine |
| (g) N-methyl-N-ethyl amine |
| (h) di-(β-methoxy-ethyl)amine |
| (i) di-propyl amine |

(i) 38.5 parts of 4,4'-diamino-6,6'-dimethylsulphonyl-stilbene-3,3'-disulphonic acid are suspended in 500 parts by volume of pyridine and 40 parts of pulversized 4-nitrobenzoyl chloride are added to the suspension while stirring at room temperature. The temperature spontaneously rises to 50–60°C and the reaction mixture thickens into a stiff yellow paste. The mixture is then heated to 110° within 30 minutes and, after it can no longer be stirred, it is cooled to 30°C. After the addition of 700 parts by volume of abs. toluene the mixture can again be stirred and it is heated to 110–115° while stirring and then refluxed for 30 minutes at this temperature while stirring. The yellow slurry obtained is cooled to 30°C, filtered under suction and the residue is washed with benzene. The yellow filter cake is then suspended in 2000 parts of 0.1% sodium carbonate is added at 70–80°C while stirring until phenolphthalein paper remains red, any benzene and pyridine present being removed by bubbling steam.
through and, after cooling, the yellow reaction product of the formula

![](image)

is filtered off and washed with 2.5% sodium chloride solution.

(ii) 200 parts of cast iron powder are suspended in 6000 parts of water, 40 parts by volume of acetic acid are added and the whole is heated for 30 minutes at 80–90° while stirring. The damp yellow filter cake of the dinitro compound mentioned above is added to the iron suspension at 90–95° and within 30 minutes and the reaction mixture is then stirred for 3 hours at the boil. After this time, 15% sodium carbonate solution is added until the pH of the mixture is 8–9 and then the iron residue is filtered off hot and is washed with hot water until the filtrate has, for practical purposes, no more diazo reaction. A yellow solution is obtained which contains the N,N′-bis-(p-aminobenzoyl) compound of the sodium salt of 4,4′-diamino-6,6′-dimethylsulphonyl-stilbene-3,3′-disulphonic acid.

(iii) Acetic acid anhydride is added dropwise to the amine solution obtained while stirring at 80–85° until a sample shows no diazo reaction. After neutralising with aqueous sodium hydroxide solution, the disodium salt of the N,N′-bis-(p-acetylaminobenzoyl) derivative formed is obtained as a whiteish precipitate which can be filtered after addition of the same volume of 25% sodium chloride solution. After cooling, it is filtered off under suction, washed with 2% sodium chloride solution and dried in vacuo at 70–80°. A yellowish powder is obtained which dissolves in hot water and can also be used for the optical brightening of cellulose fibres.

By using, instead of acetic acid anhydride, chloroacetic acid anhydride, β-bromopropionic acid anhydride or 4-methylphenoxyacetic acid anhydride and otherwise following the procedure given in Example 62, the corresponding bis(chloro-acetylamino), and bis-(β-bromopropionylamino) or bis-(4-methyl-phenoxyacetylamino) compound, respectively, are obtained which have the same effect.

To produce the urethane derivative:

![image](image)

which is an equally effective brightener, chloroformic acid ethyl ester is added dropwise at 75–80° while stirring to the solution of the sodium salt of 4,4′-bis-(p-amino-benzoylamino)-6,6′-dimethylsulphonyl-stilbene-3,3′-disulphonic acid and the acid liberated is neutralised with sodium carbonate solution. When no more diazo-izable amino groups can be traced, the reaction product is precipitated in a form which can be filtered by the addition of sodium chloride.

Both the diacetyl derivative as well as the urethane derivative are considerably more stable to sodium hypochlorite than the corresponding derivatives of 4,4′-bis-(p-amino-benzoylamino)-stilbene-6,6′-disulphonic acid.

Products of similar good brightening properties, and especially of good fastness to chlorine are obtained by repeating Example 62, and using 4,4′-diamino-6,6′-dimethylsulfonyl-stilbene-3,3′-disulphonic acid or one of the other starting acids listed following Example 1 under (b) to (s) inclusive, or 4,4′-diamino-6,6′-bis-dimethyl-

(iii) an equimolar amount of one of the acylating agents listed in Examples 4 to 50, inclusive, or by an equimolar amount of one of the acetoxy-substituted acyl halides and chloroformates listed in examples 51 to 60 with subsequent saponification or with subsequent reaction with ethylene chlorohydrin as in Example 51 or one of the bromides listed in Examples 55, 56, 58, 59 and 60.

The chloride-fastness of the compounds produced according to Example 62 and the above described variations thereof, is particularly surprising, because one would have expected that the outer —NH—CO-bridges would be particularly susceptible to the attack of chlorine, as it occurs in modern detergent mixture which contain at the same time chlorine-yielding bleaching agents.

**EXAMPLE 63**

<table>
<thead>
<tr>
<th>Parts</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecyl sulphate</td>
<td>8</td>
</tr>
<tr>
<td>Dodecylbenzene sulphonate</td>
<td>11</td>
</tr>
<tr>
<td>Sodium tripolyphosphate</td>
<td>11</td>
</tr>
<tr>
<td>Tetrasodium pyrophosphate</td>
<td>17</td>
</tr>
<tr>
<td>Sodium sulphate</td>
<td>37</td>
</tr>
<tr>
<td>Brightener according to Example 2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

are worked into a paste with 170 parts of water. The paste is dried at 60° and then milled.

6 parts of this washing powder are dissolved at 70–80° in 1000 parts of water and 0.5 part of a sodium hypochlorite solution, corresponding to 0.5 part of active chlorine, are added. After leaving for 30 minutes, uncolored cotton fabric is washed (liquor ratio 1:30) for 30 minutes at 80° in the washing liquor so obtained, then rinsed and dried. A beautifully brightened fabric is obtained.

**EXAMPLE 64**

Cotton cretonne fabric is washed for 20 minutes at 60°

(liquor ratio 1:30) in a washing liquor which contains, per liter, 5 g. of a washing agent of the composition:

<table>
<thead>
<tr>
<th>Parts</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium pyrophosphate</td>
<td>55</td>
</tr>
<tr>
<td>Dodecylbenzene sulphonate</td>
<td>30</td>
</tr>
<tr>
<td>Sodium dichloroisocyanurate (chlorine content 30%)</td>
<td>15</td>
</tr>
<tr>
<td>Brightener mentioned in Example 62</td>
<td>0.22</td>
</tr>
</tbody>
</table>

After rinsing and drying, a fabric having a neutral white appearance is obtained.

**EXAMPLE 65**

A mixture of 4.7 parts of sodium chloride, 0.3 part of lithium hypochlorite and 0.011 part of the brightening agent mentioned in Example 2 are dissolved at 60° in 1000 parts of water. If uncolored cotton cretonne fabric is treated for 20 minutes at 60° with this solution, liquor
ratio 1:30, then after rinsing and drying, cotton fabric of a high degree of whiteness is obtained.

If a treatment liquor is used in an analogous manner which contains no lithium hypochlorite, then a fabric is obtained the brightening effect of which, fluorometrically measured, is only 6% higher than that of the fabric brightened in the presence of hypochlorite.

On using the analogous derivative of 4,4'-diaminostilbene-6,6'-disulphonic acid in the described manner in the presence of 0.3 part of lithium hypochlorite, the measured fluorescence effect shows a 30% drop.

EXAMPLE 66

10 parts of white cotton household linen are washed for 30 minutes at 40° in 200 parts of a washing liquor which contains 5 g. per liter of nonylphenol polyglycol ether (with 12 ether oxygen atoms) and 0.005 g. of the brightener obtained according to Example 1, and then rinsed and dried. The cotton goods so washed have a considerably more white appearance than a comparative sample washed in the same liquor without brightener.

If, in this example, the washing process described is repeated 15 times then a considerable increase in the white effect can be observed without incurring an undesirable discoloration of the goods.

A brightening effect which is equally good for practical purposes is attained if the washing is performed in a washing liquor which contains 6 g. per liter of a non-ionicogenic washing agent of the composition:

<table>
<thead>
<tr>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonylphenol pentadecyl glycol ether</td>
</tr>
<tr>
<td>Sodium triopolyphosphate</td>
</tr>
<tr>
<td>Sodium pyrophosphate</td>
</tr>
<tr>
<td>Sodium silicate</td>
</tr>
<tr>
<td>Sodium sulphate</td>
</tr>
<tr>
<td>Sodium carbonate</td>
</tr>
<tr>
<td>Carboxymethyl cellulose</td>
</tr>
<tr>
<td>Water</td>
</tr>
</tbody>
</table>

0.005 g. of the brightener obtained according to Example 3, and an amount of sodium hypochlorite corresponding to 0.3 part of active chlorine. In this case too, an increase in the degree of whiteness is obtained on repeated washing without any undesirable discoloration of the goods.

I claim:

1. An optical brightener which in its free acid form is of the formula

\[
\begin{align*}
\text{R}_1 - \text{CO-} & \quad \text{XO}\text{SO}_3\text{Na} \quad \text{Ni-acyl} \\
\text{CH}=\text{CH} & \quad \text{SO}_3\text{Na} \\
\text{SO}_3\text{H} & \\
\text{CO-} \quad \text{R}_1
\end{align*}
\]

wherein each of \( \text{R}_1 \) and \( \text{R}_2 \) represents a member selected from the group consisting of

- (lower alkyl)-
- (lower alkoxy)-
- (lower alkyl)-
- (alkoxy)-wherein the alkoxy moiety has from 2 to 4 carbon atoms.

\[
\begin{align*}
\text{R}_1 & \quad \text{-(CH}_2\text{)}_n=\text{O} \quad \text{in which radicals} \quad \text{R}_1 \quad \text{and} \quad \text{R}_2 \quad \text{the substituent} \quad \text{R}_3 \quad \text{represents a member selected from a group consisting of} \\
\text{hydroxy, lower alkoxy, hydroxy-loweralkoxy, phenoxy, chlorophenoxy, bromophenoxy, lower alkylphenoxy and lower alkoxy-phenoxy,} \\
\text{R}_4 \quad \text{represents a member selected from the group consisting of hydrogen, fluorine, chlorine, bromine, lower alkyl, lower alkoxy, hydroxy-lower alkoxy and lower alkoxy-lower alkoxy,} \\
\text{R}_5 \quad \text{represents hydrogen, fluorine, chlorine, bromine, lower alkyl, lower alkoxy, hydroxy-lower alkoxy or lower alkoxy-lower alkoxy.} \\
\text{p} \quad \text{represents one of the integers 1 and 2, and} \quad \text{q} \quad \text{represents an integer ranging from 1 to 3,}
\end{align*}
\]

and in which formula

\[
X \text{ represents a member selected from the group consisting of} \\
\text{alkyl of from 1 to 5 carbon atoms; lower alkoxy-alkyl wherein the alkoxy moiety has from 2 to 3 carbon atoms; alkyl of from 1 to 2 carbon atoms substituted by phenyl, chlorophenyl, bromophenyl, lower alkylphenyl and lower alkoxyphenyl; di-lower alkyl-amino, pyrrolidino, piperidino, morpholino, lower alkyl-morpholino and hexamethylene imino; and} \\
m \quad \text{and} \quad n \quad \text{are identical integers ranging from 0 to 1.}
\]

2. An optical brightener which in the free acid form is of the formula:

\[
\begin{align*}
\text{CH}=\text{CH} & \quad \text{OCH}_2\text{H} \\
\text{SO}_3\text{CH}_3 & \quad \text{SO}_3\text{H} \\
\text{SO}_3\text{H} & \quad \text{CH}_3
\end{align*}
\]
3. An optical brightener which in the free acid form is of the formula:

4. An optical brightener which in the free acid form is of the formula:

5. An optical brightener which in the free acid form is of the formula:

6. An optical brightener which in the free acid form is of the formula:

7. An optical brightener which in the free acid form is of the formula:

8. An optical brightener which in the free acid form is of the formula:

References Cited

UNITED STATES PATENTS

2,690,435 9/1954 Savidge et al. 260—507
3,260,715 7/1966 Saunders 260—240

DANIEL D. HORWITZ, Primary Examiner.