

[54] PLURAL COATED PILE FABRIC
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[52] U.S. Cl. 161/67, 117/69, 161/62,
260/455
[51] Int. Cl. B32b 7/04
[58] Field of Search 161/62, 67; 117/69, 70,
117/138.5; 260/453, 408, 455, 556

[56] References Cited
UNITED STATES PATENTS
2,803,615 8/1957 Ahlbrecht 161/62

3,398,182 8/1968 Guenther 260/455
3,663,345 5/1972 Jaisinghani 161/67

Primary Examiner—Marion E. McCamish
Attorney, Agent, or Firm—Alexander, Sell, Steldt &
DeLaHunt

[57] ABSTRACT

Process for treating pile fabrics with fluoroaliphatic radical containing compositions in two steps to provide enhanced dry soil resistance and minimize stain bloom, and the treated pile fabrics from the process. The first treatment covers the pile substantially completely, and the second coating, which may comprise organic or inorganic adjuvants, is applied to the outer 25 percent or less of the pile.

3 Claims, No Drawings

PLURAL COATED PILE FABRIC

This invention relates to a process for preserving hand or texture in a piled fabric while at the same time providing dry soil resistance, stain resistance, cleanability and in certain embodiments, abrasion resistance.

The treatment of various textile fabrics with fluorochemicals to impart water and oil repellency has been known to those in the art for several years. For example, various fluorochemical compounds have been disclosed previously for use on textile fabrics made from natural fibers alone, such as wool, cotton, silk, etc., and also for use on textile fabrics made from natural fibers alone or in combination with certain synthetic fibers, e.g., nylon, polyester and rayon. Various fluorochemicals have also frequently been used in conjunction with crease-resistant resins, hand modifiers, water repellents and the like to improve fabric performance.

However, treatment with such fluorochemical compounds has not been useful or practical for all uses and has been especially impractical for treating fibers and fabrics which are subjected to severe abrasion and compressive forces as, for example, is normal with carpets.

Pile fabrics are here considered to include such upholstery fabrics as corduroy and velvet and pile carpets having loop piles, cut pile, tip sheared pile, random sheared pile as well as shag, plush and sculptured piles.

It has been proposed by others, e.g., U.S. Pat. Nos. 3,068,187; 3,256,230; 3,256,231; 3,277,039 and 3,503,915, to mix fluorinated polymers with non-fluorinated polymers to obtain a mixture (in a water or solvent solution or dispersion) which will impart good water and oil repellency to textiles, paper and leather. As described in those references, by mixing a relatively inexpensive, non-fluorinated polymer with a fluoroaliphatic radical containing polymer, one can obtain a relatively inexpensive textile fabric or fiber treating mixture which will impart water and oil repellency to the substrate. For economic reasons, those patents suggest using only a minor proportion of the fluoroaliphatic polymer in the mixture, i.e., the non-fluorinated polymer is primarily a diluent in the mixture.

Generally, attempts have been made by others with fluorochemical treatments to improve dry soil resistance of substrates, but such treatments are not durable to severe abrasion. Also, treatments proposed by others which resist abrasion tend to be receptive to dry soil under conditions of high compressive load. As a result, all of the prior art treatments satisfactory for apparel or upholstery fabrics failed to provide traffic-durable soil resistance, particularly to dry soil, to rugs and carpets. Generally, resistance to abrasion increases with increasing treatment level and consequently many prior art treatments sufficient to provide substantial abrasion resistance tended to stiffen the pile.

The present invention has as an aim and provides a process for producing novel soil-resistant pile fabrics and novel processes for the fluorochemical treatment of fabrics, particularly pile carpets, to impart durable stain repelling, anti-wicking and soil-resistant properties thereto. The process of the invention is useful for various types of pile fabrics such as, for example, those having fibers of polyester, polyolefin, nylon, acrylic, modacrylic, acetate (cellulose acetate), rayon (i.e., re-

generated cellulose), polyvinylchloride, wool, cotton, and mixtures thereof.

In accordance with the invention, there is provided a process for treating pile fabric which comprises two steps. In the first step, a light coating of a fluorochemical composition is applied to the entire pile, and, if desired, also to the backing. This coating is preferably applied by padding, top spraying, roll coating or other method which will assure complete coverage of the pile fiber surface at a level of about 0.05 to 0.2 percent by weight of pile fibers, at least sufficient to prevent wicking of stains through the pile. The treatment may be applied to the yarn before converting into a carpet or other fabric. A squeeze roll treatment after initial application is desirable to assure good penetration of the treatment into the pile. The fluorochemical material may be dissolved or dispersed in an aqueous or non-aqueous, i.e., organic, solvent. The treated fiber or carpet is preferably dried sufficiently to render the fluorochemical treatment insoluble or at least so slowly soluble as not to be removed by the following step or during cleaning operations. It will be recognized by those skilled in the art that a treatment such as this first step would be insufficient in itself to provide abrasion and dry soil resistance as it is at a lower level than would have been used in one step processes of the prior art. In the process of the invention, however, this step protects particularly those parts of the carpet not generally subject to abrasion. It will be seen that to achieve a level sufficient to confer abrasion resistance to the entire structure of the carpet would not only result in an uneconomic use of very large amounts of treating materials but would also render the pile so stiff as to have an unpleasant hand and to be almost bristle-like.

The second step also is the application of a fluorochemical composition, which composition may be the same as used in the first step, but in the second step the coating is applied preferentially to the outer or exposed part of the pile so as to be limited insofar as possible to the outer 25 percent by length or less thereof. The types of treating solutions used may also be aqueous or organic dispersions or solutions, although aqueous suspensions or dispersions are somewhat preferred. Fillers such as finely divided alumina, silica, and/or other material may be included. The amount of fluorochemical composition applied in the second step is about 0.1 to 0.4 percent by weight of the total pile. Inasmuch as it is restricted to 25 percent or less of the pile length, it will be evident that the coating over the twice-treated portion is much heavier and thicker than that which was applied in the first step.

The process of the invention is not restricted to any particular fluorochemical treating composition for the first step. A large number of fluorochemical materials are suitable as will become apparent from the disclosure herein. They may be polymeric or non-polymeric and are solid at about 20°-25° C. They are both water and oil repellent. Adjuvants may be added in either step for additional benefits including fungicides, bactericides, mildew preventative, antistatic agents, mothproofing materials and fiber lubricants. Adjuvants with glass transition temperatures (or melting points) above 45° C. may be used in proportions up to 10:1 with respect to fluorochemical and downward to 1:2 if solid at room temperature with glass transition temperature below 45° C.

In this process non-polymeric and polymeric fluorochemicals useful for the first step contain from about 15 to 60 percent by weight fluorine and comprise fluoroaliphatic radicals containing at least three fluorinated carbon atoms including therein a terminal CF_3 group. Among polymeric fluorochemicals which may be used, segmented polymers with fluorine content of about 15 to about 30 percent are particularly useful.

The fluorochemical compositions used for the second step contain about 15 to 60 percent of fluorine and may be non-polymeric or may be polymers with molecular weight up to and above about 20,000. They also combine fluoroaliphatic radicals containing at least three fluorinated carbon atoms including a terminal CF_3 group.

All the fluorochemicals used in the second step are normally non-rubbery, non-tacky, solid, water insoluble and preferably free from ethylenic or acetylenic unsaturation. They should have at least one major transition temperature (glass temperature or melting point) above about 45°C . Certain non-polymeric fluorochemicals as described in U.S. Pat. No. 3,398,182, are noted as being useful.

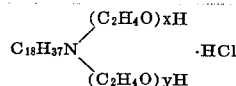
The treatment in the second step may further include as adjuvants fluorine free polymers and hard, very fine particulates such as inorganic oxides, e.g., alumina, silica, titania, silicates. Suitable sizes are particularly of the order of 1 micron and preferably less.

The following examples illustrate the best mode presently contemplated of practicing the invention. In all cases portions about 30×30 cm. are treated. Carpets are: undyed loop pile nylon carpet (18 ounces/sq. yd. or about 610 g./sq. meter pile weight), gold loop pile acrylic (about 1,100 g. per sq. meter pile weight, undyed loop pile random-shear polyester (about 1,200 g. per sq. meter pile weight) and undyed loop pile random-shear wool (about 1,200 g. per sq. meter pile weight). Two different treatments for the first step are employed and a composition for the second step is coated on the treated carpets and also, at two different levels, on carpet not subjected to the first step.

First step treatment A employs a 0.1 percent by weight solution in trichloroethylene of random copolymer of 5 percent by weight methyl acrylate, 25 percent by weight butyl acrylate and 70 percent of N-methyl perfluorooctane-sulfonamidoethyl methacrylate ($\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{CH}_3)\text{C}_2\text{H}_4\text{OCOC}(\text{CH}_3=\text{CH}_2)$). The polymer for treatment A is prepared as follows: A mixture of 48 parts of $\text{C}_2\text{F}_3\text{Cl}_3$, five parts of C_2HCl_3 , 17.5 parts $\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{CH}_3)\text{C}_2\text{H}_4\text{O}_2\text{CC}(\text{CH}_3)=\text{CH}_2$ is heated at 65°C . until solution is complete. The container is then purged with nitrogen and 0.2 parts of benzoyl peroxide added. Agitation at 65°C . is continued for 16 hours. A 32 percent solids solution is obtained. The carpet is padded to 100 percent wet pickup (55 g. solution for a piece of carpet having 55 g. pile fiber above the primary backing). After drying, the carpet is cured at 120°C . for 4 minutes.

Treatment B for the first step employs an aqueous suspension of 0.1 percent by weight of a copolymer of 10 percent by weight butyl acrylate and 90 percent by weight of N-methylperfluorooctanesulfonamidoethylacrylate ($\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{CH}_3)\text{C}_2\text{H}_4\text{OCOC}(\text{CH}_3=\text{CH}_2)$) which is padded on to 100 percent by weight of the top pile fiber and dried and cured for 5 minutes at 150°C . The suspension is made by emulsion polymerization at 80°C . under nitrogen (agitating for 16 hours) of 10 and 90

parts of the comonomers respectively in 240 parts water, 60 parts acetone using 5 parts of a commercial emulsifier "Ethoquad 18/25" with 0.5 parts 8-dodecyl mercaptan and 0.2 parts potassium peroxydisulfate. Ethoquad 18/25 is a substituted stearylamine believed to have the formula



wherein $x + y = 25$.

Treatment C for the first step employs an aqueous emulsion of 0.1 or 0.2 percent by weight of polymer solids which consist of 90 percent of the copolymer in Treatment B plus 10 percent by weight of a hybrid copolymer similar to that described in Example 19 of U.S. Pat. No. 3,574,791, here incorporated by reference.

The treatment for the second step (Treatment Q) is a top spray of 25 percent of the weight of top pile fiber of an aqueous dispersion containing (weight percentages).

0.4 percent urea

0.4 percent zirconyl chloride

1.0 percent alumina (particle size less than 45 microns)

1.6 percent of reaction product (urethane) 1:1 mole ratio of tolylene diisocyanate and N,N-bis(2-hydroxyethyl)perfluorooctanesulfonamide.

The urethane for Treatment Q is prepared as follows:

To a vessel fitted with stirrer, thermometer, condenser and heater are added 550 parts butyl acetate and 150 parts $\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{C}_2\text{H}_4\text{OH})_2$. The vessel is heated and 200 parts of butyl acetate are distilled to dry the system. The solution is cooled to 80°C . and 43.5 parts of 2,4-tolylene diisocyanate and 0.8 parts of triethylene diamine are added. Reaction is continued with stirring at 90°C . for 16 hours. The solution is cooled and to it are added 9.7 parts polyoxyethylene sorbitan monooleate and a solution of 9.7 parts $\text{C}_8\text{F}_{17}\text{SO}_2\text{NHC}_3\text{H}_6(\text{CH}_3)_3\text{Cl}$ dissolved in 530 parts of distilled water. The mixture is then agitated to form a dispersion which is converted to a stable emulsion by passage through a Manton-Gavlin homogenizer at 175 kg/cm². After drying at 70°C ., the carpet is cured for 4 minutes at 150°C . Samples are treated first with Treatments A or B and then with Treatment Q to give Samples AQ and BQ. Sample Q is a sample of carpet treated solely with Q to give urethane to 0.4 percent by weight of top pile.

Sample R is obtained by an alternative treatment of untreated carpet using the same reaction product as for Treatment Q applied by padding at 100 percent wet pickup from an aqueous dispersion containing 0.8 percent urethane.

Treatment S for the second step uses the urethane reaction product of 2 moles of N, -(2-hydroxy-ethyl)-N-ethylperfluorooctanesulfonamide and 1 mole of tolylene diisocyanate with 2 parts of polymethylmethacrylate in aqueous emulsion at levels as indicated below applied either by spray or padding (as indicated).

Treatments C and S at various levels are used together in the process of the invention and Treatment S is used alone for purposes of comparison on carpets of loop pile, nylon, random-shear polyester, random-shear wool, and random-shear acrylic. In additions,

Treatment S is used as the second step together with other first steps designated: Treatments D and E.

Treatment D employs the urethane used in Treatment Q at a 0.1 percent level alone and with 0.1 percent colloidal silica.

Treatment E uses emulsions of 0.1 percent of the copolymer of N-ethylperfluorooctanesulfonamidoethyl methacrylate and isoprene described below and 0.1 percent of a copolymer of 60 percent tridecyl acrylate and 40 percent methyl methacrylate. This treatment is used alone or with 0.2 percent dispersion of alumina.

The latter copolymer is prepared using 40 g. methylmethacrylate, 60 g. tridecylacrylate in 126 g. water and 54 g. acetone with 3.0 g. triethyleneglycol mono dodecyl ether ($C_{12}H_{25}O(C_2H_4O)_3H$), 2.0 g. of emulsifier $C_8F_{17}SO_2NHC_3H_6N(CH_3)_2HCl$ and 0.2 g. potassium peroxydisulfate by agitating under nitrogen at 50° C. for 16 hours. The product is an emulsion containing about 35 percent solids.

The fluorochemical polymer used in Treatment E is prepared as an emulsion of about 35 percent solids in 144 g. water and 36.0 g. acetone from 93.5 g. N-ethyl perfluorooctanesulfonamidoethyl methacrylate, 6.5 g. isoprene, 0.75 g. dodecyl mercaptan, 2.0 g. $C_8F_{17}SO_2NHC_3H_6N(CH_3)_2HCl$, 3.0 g. $C_{12}H_{25}O(C_2H_4O)_3H$ and 0.2 g. potassium peroxydisulfate. Equal portions of the two emulsions are blended, 8.5 percent ethylene glycol added, and this blend (about 28–30 percent solids) is then employed in Treatment E to provide the specified concentrations of polymers.

The blend used in Treatment S is an emulsified urethane and a dispersion of methyl methacrylate combined to give the desired concentrations. A solution of 86.5 g. N-(2-hydroxyethyl)-N-ethyl perfluorooctanesulfonamide and 13.5 g. 2,4-tolylene diisocyanate in 35.5 g. methyl isobutyl ketone catalyzed by 0.05 g. dibutyl tin dilaurate is heated for about 2 hours at 80° C. and then emulsified in 73 g. water using 2.5 g. $C_8F_{17}SO_2NHC_3H_6N(CH_3)_3Cl$ and 2.5 g. polyoxyethylene sorbitan monooleate by twice running through a Manton-Gaulin homogenizer at 75° C. and 135–160 atmospheres pressure. The polymethyl methacrylate emulsion is prepared under nitrogen in 100 g. water, 7.5 g. cetyldimethylbenzylammonium chloride, 10 g. methyl methacrylate, 0.2 g. potassium peroxydisulfate, stirred at 50° C. until polymerization starts, and heated to 75° C. with continuing agitation; 90 g. methyl methacrylate is then added slowly over about 2 hours. An approximately 45 percent solids emulsion is obtained.

Treated carpet samples are subjected to a series of tests in evaluating the effectiveness of the several treatments in comparison with one another and with controls:

I. Oil repellency is tested by American Association of Textile Chemists and Colorists test 118–1966T.

II. Water repellency is tested by placing a few drops of a 70:30 mixture of water: isopropanol on the sample. If the liquid beads up, the sample passes; if the liquid is absorbed in less than 10 seconds, the sample fails.

III. Stain impact resistance is tested by dropping 3 ml. of a staining solution, either a blue-dyed aqueous stain or red-dyed safflower oil from a height of 50 cm. on the sample. If the stain solution has beaded up and has not wicked out beyond 12 mm. on the pile fiber next to the primary backing after 1 minute, the test is passed; otherwise, the sample fails.

IV. Original soil resistance is determined during a walk-on test, American Association of Textile Chemists and Colorists Test 122–1967T which is rated visually. During about 5 days of daily rotation and vacuum cleaning, samples are walked on by about 6,000 persons in normal traffic and rated on the scale:

- 8 — no visible soil buildup
- 6 — slight soil buildup
- 4 — much less soil buildup than untreated
- 2 — less soil buildup than untreated
- 0 — same soil buildup as untreated

Treated samples are shampooed before any soiling using a commercially available rug shampoo ("Blue Lustre") and a mechanical shampooing machine to determine stability of the treatment, and soil resistance is determined by the above walk-on test. Samples are rated to provide the figures referred to as "Soil after Shampoo."

V. Stain bloom is determined from samples tested for stain resistance above by removing the excess staining liquid by blotting and then cleaning using a commercial paste cleaner ("Texize K-2R") and thereafter subjecting the sample to walk-on test as above and rating using the "Deering Milliken Research Corp. Soil Release Replica" from AATCC Test 130–1969. In this rating system, 1 represents severe blooming, and 5 negligible blooming.

A comparison of Samples AQ, BQ, Q and R with untreated carpet is given in Table I.

TABLE I

Sample	NYLON CARPET TREATMENTS			
	Oil Repel.	Water Repel.	Stain Resistance	Soil Resistance
untreated	0	fail	fail	0
AQ	5	pass	pass	6
BQ	5	pass	pass	6
Q	4	pass	fail	6
R	4	pass	pass	3

It will be seen that Samples Q and R which lack the overall coating of the first step of the process of the invention are unsatisfactory in one respect or another.

Carpet samples treated first by padding and squeeze-roll for the first treatment (C), and then with top-spraying for the second treatment (S) at the levels indicated are tested for oil and water repellency before and after walk-on tests as well as for soil resistance before and after shampooing, stain impact resistance and stain bloom. In all cases, treated samples passed tests for water repellency before and after a walk-on test. The results of other tests are summarized in Table II.

TABLE II

Treatment	Carpet Type	Initial Oil Repel- lency	Oil Repel- lency After Walk-on	Initial Soil Resis- tance	Soil After Sham- poo	Oil Stain Bloom
0.2% C	nylon	6	4	6	5	5
0.75% S	polyester	5	1	5	4	5
	wool	6	1	5	4	5
	acrylic	5	2	6	5	5
0.1% C	nylon	5	3	6	5	5
0.75% S	polyester	5	1	5	4	5
	wool	6	1	5	4	5
	acrylic	5	4	6	5	5
0.1% C	nylon	6	3	6	5	5
0.38% S	polyester	5	1	5	4	5
	wool	6	1	5	4	5
	acrylic	6	3	5	5	5
0.1% C	nylon	6	5	6	5	5
0.25% S*	polyester	6	4	5	4	5
with 0.16% colloidal	wool	6	1	5	4	5
Al ₂ O ₃	acrylic	5	5	5	5	5
untreated	nylon	0	0			
	polyester	0	0			
	wool	0	0			
	acrylic	0	0			

S* Using only the urethane moiety of Treatment S, without added polymethyl methacrylate.

Treatments D and E are padded into samples of carpet above and together with colloidal mineral filler and a second treatment of Treatment S is top-sprayed. Tests on the samples are summarized in Table III. All treated samples passed water repellency and oil and aqueous staining tests except as indicated.

Table IV compares the results of tests similar to those above on carpets which were treated solely with Treatments S (the second step of the invention) applied at different levels and by different methods. Except as indicated by footnotes to the table, *c*, *a* and *b* respectively, these passed water repellency tests after

TABLE III

Treatment	Carpet Type	Initial Oil Repel- lency	Oil Repel- lency After Walk-on	Initial Soil Resis- tance	Soil After Shampoo
0.1% D	nylon	5	3	6	5
0.75% S	acrylic	5	4	5	5
0.1% D plus 0.1% colloidal silica 0.75%	nylon	6	5	6	6
	acrylic	5	4	5	5
0.1% E	nylon	5	4	6	5
0.75% S	acrylic	5	4	4	4
0.1% E plus 0.2% colloidal Al ₂ O ₃ 0.75% S	nylon (a)*	5	4	6	5
	acrylic	6	4	3	3

(a)* Failed water repellency test after walk-on.

TABLE IV

Treatment	Carpet Type	Initial Oil Repel- lency	Oil Repel- lency After Walk-on	Initial Soil Resis- tance	Soil After Sham- poo	Oil Stain Bloom
0.38% S sprayed	nylon (a,b)	5	2	6	4	1
	polyester (a,b,c)	4	1	5	4	2
	wool (a)	4	1	5	2	2
	acrylic (a,b)	5	4	6	5	1

Table IV—Continued

Treatment	Carpet Type	Initial Oil Repel- lency	Oil Repel- lency After Walk-on	Initial Soil Resis- tance	Soil After Sham- poo	Oil Stain Bloom
0.75% S sprayed	nylon (a,b)	5	3	6	5	1
	polyester (a,b)	3	2	5	4	1
	wool (a)	5	1	5	4	2
	acrylic (a,b)	5	4	6	5	1
0.6% S padded	nylon	4	1	4	2	5
	polyester (c)	4	1	5	3	5
	wool	5	0	5	2	5
	acrylic	4	3	4	3	5
1.5% S padded	nylon	5	3	6	4	5
	polyester	5	2	5	4	5
	wool	6	1	6	4	5
	acrylic	5	4	4	4	5
3.0% S padded	nylon	5	4	6	4	5
	polyester	5	3	5	4	5
	wool	6	2	6	5	5
	acrylic	5	4	6	5	5
untreated	nylon					1
	polyester					1
	wool					2
	acrylic					1

a Failed oil staining
b Failed aqueous staining
c Failed water repellency after walk-on test

walk-on and also oil and aqueous staining tests. All passed water repellency test initially. It will be seen that a sprayed Treatment S was not satisfactory as a single step process except at the uneconomically high levels of 1.5 and 3.0 percent solids on the pile at which levels, moreover, the carpet was unacceptably harsh and stiff.

What is claimed is:

1. A pile fabric comprising a backing and pile fibers attached to said backing at their proximal ends and exposed at their distal ends, said pile fibers having a first coating consisting essentially of fluoroaliphatic radical containing component constituting about 0.05 to 0.2 percent by weight of the pile fiber weight of said fabric and substantially completely covering their entire

lengths and a second coating consisting essentially of fluoroaliphatic radical containing component constituting about 0.1 to about 0.4 percent by weight of the pile fiber weight of said fabric over not more than 25 percent of their length at the exposed distal ends of said pile fibers, said fabric having enhanced and durable dry soil resistance and resistance to stain wicking and penetration.

2. A pile fabric according to claim 1 wherein the second coating comprises fluoroaliphatic radical free organic adjuvant solid at 20° C. and having a glass transition temperature no lower than 45° C.

3. A pile fabric according to claim 1 wherein the second coating comprises ultrafine inorganic adjuvant.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,816,229

DATED : June 11, 1974

INVENTOR(S) : Chester J. Bierbrauer

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 7, Table III, fifth line under heading Treatment,
"silica 0.75%" should read as -- silica 0.75% S -- .

Signed and Sealed this

sixth Day of *April* 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,816,229

Dated June 11, 1974

Inventor(s) Chester J. Bierbrauer

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

The inventors name -- Bierbrauber-- should read as:
— Bierbrauer —.

Signed and sealed this 17th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents