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AQUEOUS TRANSFER OF DYE FROM WATER SOLUBLE FILAMENT TO WATER INSOLUBLE FILAMENT BLENDED THEREWITH

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16 Claims

ABSTRACT OF THE DISCLOSURE

Process for effecting randomly distributed coloration of textile materials is provided comprising applying to textile materials at least one water-soluble coloring material comprising a water-soluble polymer containing a colorant which exhibits greater affinity for the textile material than for said polymer and is capable of coloring said textile material; heating the resulting textile material while in a wet state to effect migration of the colorant from the water-soluble coloring material to the textile material with resultant random coloration of said textile material, and thereafter removing the water soluble portion of said coloring material from the textile material.

This invention relates to processes for making textile materials exhibiting a randomly distributed coloration. More particularly, the invention relates to processes for making randomly colored textile materials comprising applying water-soluble coloring materials containing a colorant, for example, a dye or pigment, to the textile materials and effecting migration of the colorant from the water-soluble materials to the textile materials by heating the treated textile material while in a wet state.

Many methods have been heretofore employed to obtain randomly distributed coloration of textile materials. As employed herein, the phrase "randomly distributed coloration" of textile materials is intended to encompass textile materials exhibiting a speckled, mottled or sprinkled coloration generally, although not necessarily, involving multiple colors. In all instances, however, the coloration is randomly distributed throughout the textile material. For example, textile materials in the form of yarns or fabrics have been manufactured by blending or doubling at least two differently colored fibers. However, the color tone of the resulting textile materials has been found to undergo undesirable changes when said textile materials are rubbed and one of the colored fibers comprising the textile materials falls out. The problem is most acute when natural fibers and synthetic fibers are differently colored and are blended. The undesirable change in color tone is quite apt to occur because the colored natural fibers fall out easily. Also, it is difficult to obtain randomly distributed coloration of textile materials having a desired color tone, especially a multi-color effect, by simply blending or doubling differently colored fibers or yarns. Generally, complicated control of blending or doubling is required. Furthermore, such complicated methods are commercially undesirable in comparison with effecting random coloration of the textile materials by simply and directly sprinkling or spraying said textile materials with a colorant solution.

Randomly distributed coloration of textile materials has been heretofore obtained by sprinkling or spraying a colorant solution on the surface of said materials. However, such methods require expensive apparatus and involve complex operations for effecting even sprinkling or spraying. Moreover, the color effect is undesirably flat and shaded away.

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Another method for effecting randomly distributed coloration of textiles comprises knitting yarn into a pre-fabric, printing color on said fabric, unravelling the pre-fabric to form yarn and thereafter producing a new fabric. The fabrics obtained in said method however, have undesirable color effects which are systematically repeated. Also, said method requires many production steps with resultant high production cost.

Accordingly, it is an object of this invention to provide methods for effecting randomly distributed coloration of textiles with deep and sharp color definition. Another object of this invention is to provide methods for effecting random coloration of textile materials, for example, yarns, woven fabrics or non-woven fabrics.

Still another object of the invention is to provide methods for effecting random coloration of textiles with a multi-color effect.

Yet another object of the invention is to provide an improved method of random coloration which comprises applying a water-soluble coloring material containing a colorant to a textile material and migrating the colorant from the water-soluble material to the textile material.

A further object of the invention is to provide an improved method of random multiple coloration, in which each colorant is easily applied to textiles and the color effect is easily controlled.

These as well as other objects are accomplished by the present invention which provides a process for effecting randomly distributed coloration of textile materials comprising applying to textile materials at least one water soluble coloring material comprising a water soluble polymer containing a colorant which exhibits greater affinity for the textile material than for said polymer and is capable of coloring said textile material; heating the resulting textile material while in a wet state to effect migration of the colorant from the water soluble coloring material to the textile material with the resultant random coloration of said textile material, and thereafter removing the water soluble portion of said coloring material from the textile material.

It has been found in the present invention that the colorant included in the water-soluble material is capable of migrating from the water-soluble material to the water-insoluble textile material to which said water-soluble material containing the colorant, for example a dye or pigment, is applied. Migration is effected when the treated textile material is heated while still in a wet state and said water-soluble material is swelling. It has been found that said migration occurs easily when water-soluble materials, in the form of chips, scales, granules or fibrous materials are used.

The water-soluble coloring materials employed in the present invention are formed from water-soluble polymers, for example, polyvinyl alcohol, polyvinyl alcohol derivatives, sodium alginate, starch, sodium salt of carboxymethyl cellulose, acetylated starch, hydroxyethyl cellulose, sodium salt of carboxymethyl starch and the like.

The water-soluble coloring materials can be used in the form of chips, scales, granules or fibrous materials, for example, short-cut fibers, staples, continuous filaments. Especially preferred water-soluble coloring materials are in the form of fibrous materials.

The water-soluble coloring materials in the form of filaments can be manufactured by conventional techniques employed for fiber making. For example, a preferred method comprises preparing an aqueous solution of a water-soluble polymer as an aqueous spinning solution, extruding the spinning solution into a coagulating bath or dry air, preferably hot air, through a spinning nozzle and drawing and/or heat-treating the extruded filaments, if desired.

Another method of making the water-soluble coloring materials in fibrous form comprises extruding an aqueous solution of a water-soluble polymer through a slit for forming a film, coagulating, drawing and/or heat-treating and thereafter cutting, slitting or splitting the film to obtain flat tapes, scales or split fibers.

In the above-mentioned methods, the temperature at which the fibrous coloring materials will dissolve or swell in water can be easily controlled by variations of the draw-ratio of the coagulated materials, the temperature of heat-treatment or the treating times.

These methods can be advantageously employed to obtain water-soluble materials exhibiting the dissolving or swelling temperatures required in the subsequent steps of the process of the present invention. The dissolving temperature of the water-soluble materials can be also varied in accordance with the properties of the colorants or textile materials employed. The water-soluble fibrous coloring materials obtained by the above methods are advantageously applied by blending or doubling with other textile materials, for example, staple fibers, filaments, webs, slivers, tows, threads. Furthermore, these fibrous materials can be cut, if desired, to prepare the water-soluble coloring materials in the form of short-cut fibers or powders.

In these methods, it is possible to change the form or size of the water-soluble coloring materials by varying the form or size of the extrusion die or spinneret employed. An especially preferred polymer for use as the water-soluble coloring material in accordance with the present invention is polyvinyl alcohol. Said polymer can be easily formed into filaments or films and the dissolving temperature of the resulting materials can be easily controlled.

Furthermore, the water-soluble materials can be obtained by cutting or reducing sheets, films or blocks of the water-soluble coloring materials. The water-soluble coloring materials obtained in said method can be obtained in the form of chips, scales, granules or powders. In this case, since the size of the materials thus obtained is irregular, varied color effects can be obtained. However, it is not easy to control the state or extent of the dissolving or swelling of these water-soluble materials in water. Therefore, it is considered advantageous for the water-soluble coloring materials to be made by the fiber or film-forming processes.

The colorants can be incorporated in the water-soluble materials to form the water-soluble coloring materials by various methods. For example, the colorants can be mixed in the above-mentioned aqueous solution of the water-soluble polymers by either dissolving or dispersing said colorants therein prior to extrusion. If desired, dyeing auxiliaries such as wetting or dispersing agents can also be employed.

Furthermore, the water-soluble coloring materials containing the colorant can be obtained by applying the colorant to the water-soluble materials, for example, by coating or impregnating the fibrous water-soluble material with a solution or dispersion of the colorant. In this invention, the water-soluble coloring materials which are obtained by extruding an aqueous solution of water-soluble polymers admixed with the colorant is especially preferred for deeply and sharply coloring the textiles.

The colorants employed in the present invention must have an affinity for the textile materials only; colorants having affinity for the water-soluble polymers forming the coloring materials cannot be used. If the colorant interacts in some manner with the water-soluble polymers, it is difficult to produce said coloring materials and the colorant will not migrate from the water-soluble materials to the textile. Therefore, for example, combinations such as the sodium salt of carboxymethyl cellulose containing primary hydroxyl groups or sodium alginate and reactive dyestuffs cannot be employed.

The colorant content in the water-soluble coloring material is at least 3% by weight, and preferably more than 5% by weight for deep and sharp coloring. Said colorant content is higher than the content of the colorant generally added to the spinning solution for manufacturing dope-dyed fibers.

The water-soluble coloring materials can be applied to the textile materials by the following methods:

One method comprises blending or doubling and twisting the fibrous coloring materials with textile materials, for example, in the form of staple fibers, filaments, yarns, tows, slivers or webs. This method can be conducted in a conventional manner, for example, mixing, spinning, doubling and twisting or wrapping. In such methods, the fibrous coloring materials impart an interesting coloration to textiles. For example, thermoplastic yarns blended with the fibrous coloring materials can be crimped to obtain randomly colored textured yarn by using conventional means such as false-twisting. In these cases, the content of the coloring materials in the textured yarn is preferably less than 40 wt. percent, especially 1 to 30 wt. percent, for imparting sharp coloration to the yarns.

Of course, two or more of the coloring materials each having different colorants can be used to obtain multi-coloration.

Other methods for applying the coloring materials to the textile materials can be employed, for example, dipping the textile materials into a dispersion or solution of the coloring materials or spraying or coating the textile materials with a dispersion or solution of the coloring materials.

In these instances, the coloring material is preferably in a finely divided state, for example, scales, chips, granules, powders or short cut fibers. These materials can be dispersed in water alone by conventional means. These coloring materials, however, must not dissolve in the water before being fixed to the textile materials. Therefore, when employing the above-mentioned method, the coloring materials employed must have a dissolving temperature higher than the temperature of the water used in the dispersion. For example, when the coloring materials are dispersed in water at room temperature, said materials must have a dissolving temperature of about 40° C. to 90° C. or higher. Under these conditions, the water-soluble materials in the dispersion swell without dissolving out in the water. In this form, the dispersion is quite cohesive to textile materials and when the textile materials are treated by the dispersion, the coloring materials can be easily fixed to the surface of the textile materials.

Another method for applying the coloring materials to the textile materials can be conducted by adhering the coloring materials to the surface of the textile materials, for example, by conventional static flocking means or by coating or printing the mixture of the coloring materials or the dispersion of said materials and other water-soluble adhesives onto the textile materials.

Furthermore, the water-soluble materials can be applied by blending or mixing in the webs for non-woven fabrics as the textile materials.

After the water-soluble coloring material has been applied to the textile material, the resulting textile material, while in a wet state, is heated to swell the water-soluble materials and effect migration of the colorant from the coloring materials to the textile materials. This heat-treatment can be generally conducted by such conventional means as by steaming such as with raw steam, high pressure steam or superheated steam. When the heat-treatment is effected by steaming, the textile materials in the form of yarns, tows, slivers and the like are preferably treated in the form of wound layers, for example, in the form of a cheese or cone.

In an alternative method, the treated textile materials can be dampened and thereafter heated. After application of the dispersion of the coloring materials to the textile

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materials, the treated textiles can be directly heated without drying. The heat-treatment must be conducted at a sufficiently high temperature to cause swelling of the coloring material and migration of the colorant from the water-soluble material to the textile materials.

Effective temperatures for causing migration of the colorant and coloring the textile commence at the least 100° C., and preferably at at least 120° C.

Employing the above processes, textile materials are given a deep and sharply defined random in coloration.

Upon completion of the above-described heat-treatment, said colored textile materials are treated with an aqueous solution maintained at a temperature higher than the dissolving temperature of the water-soluble coloring materials for removing the water-soluble portions thereof remaining on the surface of the textiles. It is desirable to add an accelerator for dissolving the coloring mediums in the dissolving solution, for example, organic acids, inorganic acids, bases, phenols, hydrogen peroxide or zinc chloride.

It is possible to apply the method of the invention at almost any point in the overall process from the production of the initial fibers to the completed yarn or fabrics.

In the method of the invention, it is easy to apply the colorant to the textile materials by using the water-soluble materials as a coloring medium.

The textile materials obtained in accordance with the present invention exhibit deep and sharp randomly distributed coloration. The randomly distributed coloration effect of the textile materials can be easily changed by

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polymerization: 1700) and Sumikaron Red FB (C.I. Disperse Red 60) which was dialyzed for one day by using parchment paper, at a weight ratio of 100:15, and thereafter adding water to the mixture to obtain a weight ratio of water:spinning solution of 60:40. Filaments were formed from said spinning solution by extruding said solution into hot air at 110° C. and drawing said filaments in a ratio of 1:4.0 at 150° C. in a heated air zone. The size of the filaments obtained by the above-described method was about 20 deniers and said filaments exhibited a dissolving temperature of 70° C.

The resulting colored filaments were employed as water-soluble coloring materials and were doubled and twisted in 70 turns per meter with a textured yarn of polyester filaments (150 d./32 f.) and wound up in the shape of a cone.

Thereafter, the twisted yarn wound up in cone form was treated by means of steaming at 130° C. for 30 minutes and dipping in water at 100° C. for a period of 15 minutes, whereby the polyvinyl alcohol remaining on the yarns was dissolved off. Thereafter, the textured yarns were subjected to hydro-extraction and drying after reduction and clearing treatment.

The textured yarns obtained by this method exhibited a randomly distributed color effect in red with excellent white resistance.

EXAMPLE 2

Water-soluble filaments A to D containing a colorant were produced by using polyvinyl alcohol (PVA) as a starting material under the conditions shown in Table I.

TABLE I

Sample.....	A	B	C	D
Starting PVA:				
Degree of polymerization.....	1,700.....	1,700.....	1,700.....	1,700.....
Degree of saponification (percent).....	97.5.....	97.5.....	99.8.....	99.8.....
Dope:				
PVA concentration in aqueous spinning solution (percent).....	45.0.....	40.0.....	40.0.....	40.0.....
Coloring agent.....	Sumikaron Yellow FG (C.I. Disperse Yellow 8) C.I. 12690.	Suminol Milling Red GW (C.I. Acid Red 276).	Sumiacryl Blue 3R (C.I. Basic Blue 47).	Sumikaron Red FB (C.I. Disperse Red 60).
Coloring agent content to PVA (weight percent).....	10.....	10.....	10.....	15.....
Temperature of spinning solution (° C.).....	140.....	135.....	135.....	90.....
Spinning:				
Spinning temperature (° C.).....	120.....	100.....	110.....	80.....
Spinning operation.....	Dry spinning system..	Dry spinning system..	Dry spinning system..	Wet spinning system. ¹
Drawing:				
Draw ratio.....	4.....	4.....	4.....	4.....
Drawing temperature (° C.).....	150.....	150.....	150.....	80.....
Heat-treatment:				
Temperature (° C.).....	150.....
Treating times (seconds).....	30.....
Property of filaments:				
Deniers/filaments.....	20/1.....	15/1.....	30/1.....	35/3.....
Dissolving temperature in water (° C.).....	70.....	65.....	80.....	80.....

¹ A solution of Glauber salt is used as coagulating bath.

altering the size or form of the water-soluble coloring materials containing the colorant.

It is a major advantage of the present invention to be capable of imparting the randomly distributed color effect to a variety of yarns by simple operations.

For example, randomly distributed coloration of textured yarns has heretofore been unattainable, however, the method of the present invention makes possible the obtainment of said textured yarn exhibiting randomly distributed coloration.

Furthermore, in accordance with the present method, randomly distributed multi-coloration of textiles is easily obtained by using two or more water-soluble coloring materials containing different colorants.

The following examples further illustrate the present invention without restricting the invention to the specific details actually shown. Unless otherwise specified, all percentages and parts are by weight.

EXAMPLE 1

A spinning solution was prepared by admixing polyvinyl alcohol (degree of saponification: 99.8%, degree of

Thereafter, each filament was doubled and twisted with yarn and further treated as shown in Table II.

TABLE II

	Sample			
	A	B	C	D
	Nylon filament yarn 134 d./34 f.	Worsted yarn (40' S)	Polyacrylic spun yarn (40' S) ¹	Mixed spun yarn of polyester and cotton (45' S)
Textile Material.....
Doubling (turns/meter).....	28.....	28.....	28.....	70.....
Steaming:				
Temperature (° C.).....	100.....	100.....	100.....	130.....
Treating times (minutes).....	15.....	20.....	10.....	30.....
Removing:				
Temperature (° C.).....	90.....	90.....	95.....	95.....
Treating times (minutes).....	10.....	10.....	10.....	15.....

¹ Dyed with Sumiacryl Red (C.I. Basic Red 18).

The results obtained are shown in Table III.

TABLE III

Textile materials:	Randomly distributed color combination
Nylon filament yarn	White and yellow.
Worsted yarn	White and red.
Polyacrylic spun yarn	Red and blue.
Mixed spun yarn (polyester and cotton)	White and red.

EXAMPLE 3

Three coloring materials were produced in accordance with the method for making sample A in Example 2, by using each of Sumikaron Red FB, Sumikaron Yellow and Sumikaron Blue GG (Anon). The three coloring materials were respectively applied to nylon filament yarn and colored by the same method employed in Example 2. The resulting yarns exhibited randomly distributed coloration in a combination of red, yellow, blue and white.

EXAMPLE 4

The coloring material obtained by the method of Example 1 was twisted in 150 turns per meter with a polyester spun yarn colored in blue by using Resolin Blue FBL (C.I. Disperse Blue 56). The twisted yarns were knitted into a fabric. Thereafter, said knitted fabric was treated by means of steaming at 120° C. for 30 minutes and then was dipped in water at 100° C. for a period of 5 minutes to remove the water-soluble portion of the coloring materials. Thereafter, the resulting fabric was soaped, rinsed and dried. The resulting fabric exhibited randomly distributed coloration in blue and violet and the color effect shows a shot effect.

EXAMPLE 5

Three coloring materials of the type employed in Example 3 were cut in lengths of 10 mm. and blended with polyester fibers (3 deniers, length of 38 mm.). A mixed spun yarn of said coloring materials and polyester fiber was produced by conventional means. The yarn was treated by means of steaming at 130° C. for 30 minutes and the water-soluble polyvinyl alcohol portion of said coloring materials were sufficiently removed by treatment with hot water. The resulting spun yarn exhibited a randomly distributed multi-colored effect in red, blue and yellow.

EXAMPLE 6

The three coloring materials used in Example 5 were dispersed in water at 50° C. In this case, the concentration of each of the coloring materials was 0.25%. The polyester spun yarn was soaked in said dispersion to apply the swelled coloring materials to the yarn. The treated yarn was then hydro-extracted. This yarn was further treated by means of steaming at 130° C. for 30 minutes and dipped in hot water to remove the polyvinyl alcohol from the yarn. The resulting yarns were brilliantly and randomly multi-colored with good color fastness and good white resistance.

EXAMPLE 7

Water-soluble coloring materials E and F were produced in filament form under the conditions shown in Table IV.

TABLE IV

	E	F
Dope:		
Initial material	Sodium alginate	Sodium salt of carboxymethyl cellulose.
Initial material concentration in aqueous spinning solution (percent).	20	60.

TABLE IV—Continued

	E	F
Dope:		
Colorant and others	(C.I. Direct Red 28) C.I. 22120.	Supranol Fast Red BB (C.I. Acid Red 154), oxalic acid C.I. 24800.
Colorant content relative to initial material (percent).	10	8.
Spinning:		
Spinning operation	Wet spinning	Dry spinning.
Coagulating bath	Acetone	Hot air (110° C.).
Drawing:		
Draw ratio	1.7	4.
Drawing temperature, ° C.	150	150.
Property of coloring material:		
Deniers	35	6.
Dissolving temperature in water, ° C.	40	75.

Thereafter, said coloring materials were twisted with textile yarns and said textile yarns were randomly colored as shown in Table V.

TABLE V

Coloring material	E	F
Textile yarn	Cotton spun yarn	Worsted yarn.
Steaming	100° C., 20 minutes	130° C., 30 minutes.
Dissolving temperature, ° C.	80	90.

EXAMPLE 8

A film was formed by extruding an aqueous solution of polyvinyl alcohol containing Sumikaron Yellow into a coagulating bath containing Glauber's salt at 80° C. and drawing said film at a draw ratio of 5.5 at 100° C. The resulting film had a thickness of 0.13 mm. and its dissolving temperature was 85° C. The film was cut in lengths of 5 to 10 mm. and in widths of 0.2 to 3 mm. to make the coloring materials.

Thereafter, said materials were applied to polyester spun yarn in the same manner employed in Example 6. The resulting yarn exhibited randomly distributed coloration.

EXAMPLE 9

Chips were produced by pulverizing a block of polyvinyl alcohol containing Sumikaron Red FB. The block was formed by vacuum drying an aqueous solution of polyvinyl alcohol. The size of the chips was 3 mm. and their dissolving temperature was 80° C. The chips were dispersed in water containing Duck-Algin NSPL (produced by Kamogawa Kagaku Co., Ltd.; thickener) to form an 8% by weight dispersion of said chips and said dispersion of coloring materials was used as a thickener. Polyester fabric was printed with said thickener. Thereafter the printed fabric was steamed at 130° C., for 30 minutes and dipped in hot water to dissolve off the polyvinyl alcohol and thickener.

The resulting fabric exhibited randomly distributed coloration on the printed parts.

What is claimed is:

1. Process for effecting randomly distributed coloration of textile materials comprising blending filaments of a water-insoluble textile material with filaments of at least one water-soluble polymer containing at least 3% by weight of a colorant which is non-reactive with the water soluble polymer and which exhibits greater affinity for the textile material than for said polymer and is capable of coloring said textile material, to form a yarn, heating the resulting yarn in a water wet state to effect limited migration of the colorant from the water-soluble polymer to the textile material with resultant random coloration of said textile material, and thereafter removing the water soluble polymer.

2. Process as defined in claim 1 wherein said filaments of water-insoluble textile material and water soluble polymer are doubled together to form a yarn.

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3. Process as defined in claim 1 wherein said filaments of water-insoluble textile material and water soluble polymer are twisted together to form a yarn.

4. Process as defined in claim 1 wherein the filaments of water-insoluble textile material and water soluble polymer are fibers, staples, continuous filaments or mixtures thereof.

5. Process as defined in claim 4 wherein the filaments of water insoluble textile material and water soluble polymer are woven together into a web.

6. Process as defined in claim 4 wherein the filaments of water insoluble material and water soluble polymer are carded together into a silver.

7. Process as defined in claim 1 wherein the filaments of water-soluble coloring materials are doubled and twisted yarns.

8. Process as defined in claim 1 wherein the water-soluble coloring materials are doubled and twisted with crimped yarns.

9. Process as defined in claim 1 wherein the water-soluble coloring material is doubled with a textile yarn and the resultant doubled yarn is crimped.

10. Process as defined in claim 1 wherein the water-soluble coloring material comprises polyvinyl alcohol and a colorant.

11. Process as defined in claim 1 wherein fibrous water-soluble coloring materials are blended with staple fibers and the resultant blended fiber product is steamed and thereafter the water-soluble materials are removed from the colored fiber product.

12. Process as defined in claim 1 wherein the resulting textile material contains less than 40 weight percent of the water-soluble coloring material.

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13. Process as defined in claim 1 wherein at least two water-soluble coloring materials, each containing a different colorant, are employed.

14. Process as defined in claim 1 wherein the water-soluble coloring materials exhibit a dissolving temperature in water of from 40° C. to 90° C.

15. Process as defined in claim 1 wherein the resulting textile material is heated in the wet state at temperatures of at least 100° C.

16. Process as defined in claim 1 wherein the colored textile materials are treated with an aqueous solution maintained at a temperature higher than the dissolving temperature of the water-soluble coloring materials thereby effecting the removal of the water-soluble portions thereof remaining on the surface of the textile.

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DONALD LEVY, Primary Examiner

U.S. Cl. X.R.

8—29; 57—164; 28—76T, 75 WT

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,756,770 Dated September 4, 1973

Inventor(s) Seiichi Kobayashi et al

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

In the Specification:

Column 4, lines 31 and 32, delete "or spraying or coating the textile materials with a dispersion or solution of the coloring materials", (second occurrence).

Column 6, Table II column B, "40'S" should be --48'S--.

In the Claims:

Claim 6, line 3, "silver" should be --sliver--.

Signed and sealed this 13th day of August 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
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