United States Patent

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Continuation-in-part of application Ser. No. 654,857, July 20, 1967, now abandoned. This application Dec. 8, 1969, Ser. No. 882,817

[54] **DUPLICATING RIBBONS AND PROCESS**
10 Claims, 2 Drawing Figs.

[52] U.S. Cl. ..... 117/36.4, 117/138.8 N, 117/76 T
[51] Int. Cl. B41m 5/10
[50] Field of Search 117/36.1, 106, 36.4; 197/172

[56] References Cited

UNITED STATES PATENTS

3,022,880	2/1962	Newman	117/36.1
3,303,045	2/1967	Newman	117/36.1
2,898,229	8/1959	Herr et al.	117/106

Primary Examiner—Murray Katz
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ABSTRACT: Process for producing novel fabric duplicating ribbons having improved ink-receptivity formed from synthetic thermoplastic filaments, in which the ribbons are rendered more ink-receptive by contact at elevated temperatures with vapor of a compound of titanium, silicon or germanium in the presence of moisture, and are thereafter impregnated with ink.

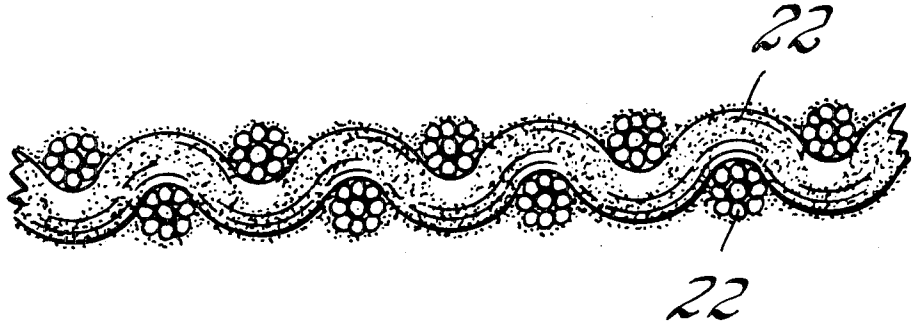


Fig. 1

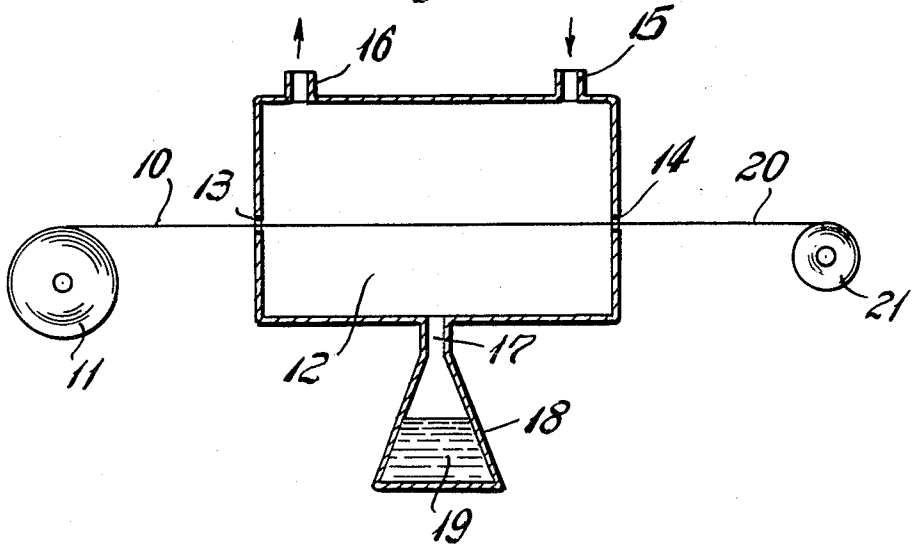
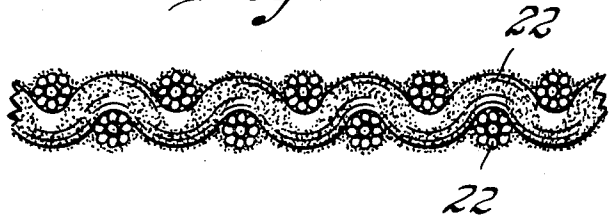


Fig. 2



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DUPLICATING RIBBONS AND PROCESS

This application is a continuation-in-part of parent application Ser. No. 654,857, filed July 20, 1967, now abandoned.

The present invention is concerned with providing fabric duplicating ribbons of improved ink-receptivity and increased ink capacity and which release ink uniformly during repeated reuse. Nearly all conventional typewriter ribbons and other duplicating ribbons of the woven or matted fabric type based upon synthetic thermoplastic filaments rely upon the thickness of the fabric or the crimping or puckering of the filaments and fabric to provide a greater number of air spaces within the fabric for retaining the liquid ink.

The synthetic thermoplastic filaments themselves are impervious to the liquid ink and in nearly all cases the smooth surface of the filaments repels the liquid ink. The lack of affinity of the filaments for the ink coupled with the fact that the ink is mainly contained in the form of droplets retained external to the filaments in air spaces between the filaments and threads causes such ribbons to release the ink too heavily during initial use and to have insufficient reusability. The initial copies are so heavily inked that they are dirty to the touch. After limited reuse the density of the typed images reduces sharply and too soon the ribbon must be replaced.

Attempts have been made to render such filaments porous to increase their ink-receptivity. This has been successful to some extent but still the surface of the filaments repels ink. Also there is the disadvantage that the porous filaments are not as strong as uniform filaments.

According to the principal embodiment of my aforementioned copending application, it is proposed to produce duplicating ribbons of increased ink-receptivity by treating the filaments with the vapor of a compound of titanium, silicon or germanium, in the presence of moisture, to form an ink-receptive coating on the filaments. Thereafter the filaments are formed into a fabric and the fabric is inked.

The aforementioned process is quite suitable for the production of a wide variety of duplicating ribbons but has been found to involve a great deal of difficulty in connection with the production of woven duplicating ribbons. The treated filaments have relatively rough, abrasive surfaces, rather than their original smooth surfaces, and therefore are very difficult to manipulate on a weaving machine without breakage. They are difficult to transport, wind, slide and weave and it is not possible to weave a uniform fabric therefrom.

It is the principal object of the present invention to overcome these problems by providing a novel method for producing duplicating ribbons from woven fabrics of synthetic thermoplastic filaments and multifilament threads whereby the woven fabrics are aftertreated so as to be more receptive to and retentive of liquid inks.

It is another object of this invention to provide duplicating ribbons of the aforesaid type which have a greater ink capacity than prior know ribbons and have an extended period of reuse due to their gradual release of ink during each use.

These and other objects and advantages of this invention will be clear to those skilled in the art in the light of the present disclosure, including the drawings, in which:

FIG. 1 is a plan view illustrating an apparatus useful for treating the present woven fabrics; and

FIG. 2 is a diagrammatic cross section, to an enlarged scale, of a woven typewriter ribbon produced according to the present invention.

The objects and advantages of the invention are accomplished by manufacturing woven duplicating ribbons in conventional manner from synthetic thermoplastic filaments and thereafter treating the woven fabric with a hydrolyzable inorganic or organic compound of titanium, silicon or germanium in the presence of moisture. It has been discovered that when such fabrics are treated in the presence or solutions of moisture with such compounds of the aforementioned compounds, the vapors penetrate the fabric to a substantial extent and hydrolyze and deposit oxides on the filament surfaces so that the affected surfaces of the filaments carry a fine oxide coating which is very receptive to and retentive of liquid ink

and which releases such ink gradually and uniformly under the effects of imaging pressure. The woven fabrics are permeable to the vapors or solutions of the hydrolyzable compounds which deposit on the portions of the filaments which they contact. It appears that the compounds completely cover all of the filaments in the fabric except at those points where the filaments are in close contact with one another.

The hydrolyzable compounds useful according to the present invention are the organic and inorganic compounds of titanium, silicon and germanium which hydrolyze fairly rapidly and completely to deposit ink-receptive coatings on the surface of synthetic thermoplastic filaments. Compounds of titanium are preferred such as titanium tetrachloride, tetrabutyl titanate, polybutyl titanate, tetraisopropyl titanate and tetrastearyl-tetraisopropyl titanate. The chlorides and other halides of germanium and silicon are also quite effective as are the corresponding tetra organo silicates.

The hydrolysis reaction is one in which the compound used, such as tetraisopropyl titanate, reacts with the moisture in the atmosphere to form a polymeric metal oxide, such as polymeric titanium dioxide, and the corresponding alcohol, such as isopropyl alcohol, as a side product. The titanium dioxide bonds strongly to synthetic thermoplastic filaments, either chemically or physically, and the alcohol is removed. In many cases, the titanium dioxide coating is a hydrated titanium dioxide, particularly when the reaction is carried out at lower temperatures. However such a coating is just as effective in obtaining the desired advantages of the present invention.

The woven fabric preferably is treated with vapors of the hydrolyzable compound at elevated temperatures. The filaments of the fabric have been oriented subsequent to extrusion, and the amount of heat applied to the fabric is insufficient to relax or disorient the polymer structure of the filaments. As shown in FIG. 1, the web **10** of woven fabric is expended from roller **11** and passes into heating tunnel **12** for contact with the vapor. The tunnel comprises openings **13** and **14** to permit passage of the web, inlet duct **15** through which hot moist air is fed into the tunnel and exhaust duct **16** through which contaminated air is evacuated from the tunnel. The tunnel is also provided with inlet tube **17** associated with vaporizing chamber **18** containing the compound **19** to be converted to vapor form. The treated web **20** exits opening **14** and is collected on takeup roll **21**. The drying tunnel is preferably provided with heating means to develop the required temperature without depending solely upon the temperature of the moist air introduced through inlet **15**. Also vaporization chamber **18** is provided with heating means and preferably with a source of forced hot dry air for propelling the generated vapor into the heating tunnel at the desired rate.

The chemical reaction involving the heated vapor and moisture is a hydrolysis in which the titanium, silicon or germanium atom combines with oxygen to form an oxide which deposits on the heated surface of the filaments of the woven web **10** and bonds strongly thereto when the filaments are cooled. It appears likely that minor amounts of hydrous titanium dioxide and oxyhalide also deposit on the filament in cases where the compound used is a halide. Similarly other impurities are apparently deposited when titanates and silicates are used. However these impurities do not interfere with the objects of the invention.

The volatile materials generated in the hydrolysis reaction are gradually removed from the drying tunnel through duct **16** as fresh, moist, hot air is continuously slowly fed into duct **15**.

The atmosphere within the drying tunnel is maintained saturated with the vapor of the compound used. The rate of entry of the vapor through inlet tube **17** may be controlled, as may the speed of the web through the drying tunnel, in order to obtain the desired oxide coating on the filaments of the web. It is generally preferred to permit the filaments to accept a very thin uniform oxide coating bonded directly to the filament surface.

The preferred woven fabrics treated according to the present invention are those comprising nylon polyamide fila-

ments, which are preferably treated at a temperature of about 200 ° C., those comprising Orlon polyacrylonitrile fibers, which are preferably treated at a temperature of about 225 ° C., those comprising rayon acetate fibers which are preferably treated at a temperature of about 168° C., those comprising saran vinyl chloride-vinylidene chloride threads, which are preferably treated at a temperature of about 100 ° C., and woven webs comprising similar filaments of synthetic thermoplastic polymers.

The following illustrates the production of a woven nylon typewriter ribbon according to the invention.

A web of conventional woven nylon typewriter ribbon fabric is selected, such as one woven from multifilament threads of 1.15 denier hexamethylene diamine-adipic acid filaments. The threads, containing 35 filaments each, are woven into fabrics having a warp count of 170 and a filler count of 115, and the woven fabric has a caliper of about 0.0042 inch.

The ribbon web is treated with titanium tetrachloride in an apparatus as shown in FIG. 1 of the drawing. The heating tunnel is heated to a temperature of 230 ° C. and hot moist air is slowly blown in through duct **15** and evacuated through duct **16**. Liquid titanium tetrachloride is present in vaporizing chamber **18** and is heated to 85° C. to cause it to vaporize. The vapors are propelled through tube **17** by a stream of forced hot dry air. When the atmosphere within the heating tunnel is saturated with the titanate vapor, the nylon web is passed therethrough at a speed of about 30 feet per minute to permit the surfaces of the filaments of the web to become heated above about 200 ° C. and receive a uniform thin covering of the hydrolyzed titanate which appears to consist essentially of titanium dioxide polymer. The coated web **20** exits the tunnel through opening **14** where it is cooled by the atmosphere and then collected on takeup roll **21**.

The coated web **20** comprises coated threads **22**, as shown in FIG. 2 of the drawing. Next the web is cut into ribbons of the desired width which are inked in conventional manner with a conventional oil- and pigment-typewriter ribbon ink to produce duplicating ribbons. Such ribbons accept a higher amount of ink than corresponding nylon ribbons which have not been treated according to the present invention, and produce cleaner, more uniform and more numerous copies than the corresponding untreated nylon ribbons.

In some cases it is preferred to treat the fabrics at room temperature and this is accomplished by passing the fabric to be treated through a solution of the hydrolyzable compound dissolved in a solvent which does not dissolve the synthetic thermoplastic polymer. Suitable solvents include isopropanol, butanol, heptane, benzene and the like. The solvent is present to dilute the solution so that excess accumulation is avoided. The amount of solvent used depends upon the speed of the fabric through the solution and the holding power of the fabric. Fabrics trap large amounts of the solution and therefore dilute solutions containing small amounts of the hydrolyzable compound are preferably used. In general, the solutions contain from 5 percent up to about 20 percent of the hydrolyzable compound.

In all cases the presence of high humidity is required for the hydrolysis reaction which may occur at room temperature but occurs more rapidly at elevated temperatures. Preferably the humidity is in excess of 80 percent relative humidity and the temperature is in excess of 100 ° C.

The titanium compounds suitable for use according to the present invention are commercially available from the du Pont Company, Wilmington, Del., under the registered trademark "Tyzor" TPT, TBT, PB, AP and others.

Variations and modifications may be made within the scope of the claims and portions of the improvements may be used without others.

I claim:

1. The process of producing duplicating ribbons which comprises the steps of:

a. impregnating a woven fabric comprising synthetic thermoplastic filaments with a hydrolyzable compound selected from the group consisting of compounds of titanium, silicon and germanium;

b. hydrolyzing said compound in said fabric in the presence of high humidity to form an ink-receptive, ink-retentive solid coating bonded to the surface of the filament of said fabric; and

c. impregnating said fabric with a liquid ink to produce duplicating ribbons.

2. The process of claim **1** in which the fabric is impregnated with the hydrolyzable compound in vapor form at a temperature in excess of 100 ° C.

3. The process of claim **1** in which the fabric is impregnated with a solution of the hydrolyzable compound in a volatile solvent and the solvent is thereafter evaporated.

4. The process according to claim **1** in which the compound is a titanium compound selected from the group consisting of titanium tetrachloride, tetrabutyl titanate, polybutyl titanate, tetraisopropyl titanate and tetrastearyl-tetraisopropyl titanate.

5. The process according to claim **1** in which the fabric comprises said filaments which are formed into the fabric by twisting a number of them together to form multifilament yarns which are woven into the fabric.

6. The process according to claim **1** in which the filaments comprise nylon.

7. A duplicating ribbon made in accordance with the process of claim **1**.

8. A duplicating ribbon made in accordance with the process of claim **4**.

9. A duplicating ribbon made in accordance with the process of claim **5**.

10. A duplicating ribbon made in accordance with the process of claim **6**.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,620,802 Dated November 16, 1971

Inventor(s) Douglas A. Newman

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

Column 1, line 20, "use" should read -- uses --; line 53, "know" should read -- known --; lines 69-72, "or solutions of moisture with such compounds of the aforementioned compounds, the vapors" should read -- of moisture with vapors or solutions of the aforementioned compounds, such compounds --; Column 3, line 5, "168° C" should read -- 160° C --.

Signed and sealed this 23rd day of May 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents