ELECTROLYTIC WATER-PROOFING OF TEXTILE FABRICS: THE TATE PROCESS.* †

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PRIOR to the advent of the electrolytic method, the art of water-proofing textile fabrics was confined to two methods: Mechanical processes and chemical processes.

Mechanical processes embrace all methods which involve direct impregnation, filling or coating the fabrics with rubber, waxes and various compounds which achieve the result of rendering them proof against the penetration of both water and air. In view of the fact that the vast majority of the uses for which textile fabrics are designed requires that they possess the quality of ventilation, all of these mechanical processes are correlatively restricted in their application and are employed most largely in association with fabrics intended for specific uses wherein air circulation is a negligible factor; when used in associations where ventilation is an essential factor, notably for wearing apparel such as raincoats, the results are unsatisfactory from the viewpoints of both comfort and hygiene.

Chemical processes embrace all methods whereby a coating of a water-repelling substance is deposited on the surfaces, yarns or fibres of textile fabrics through the media of chemical reactions. These methods are designated as follows: (1) The *aluminium soap process*; (2) the *lanolin process*; (3) the *cuprate of ammonia process*. Since the electrolytic method of water-proofing described in this paper involves the impregnation of fibres with aluminium compounds, the first of these chemical processes will be described briefly.

In the aluminium soap process, which is one of the most largely employed where ventilation is an essential factor, the fabric is first saturated with a relatively heavy solution of soap and then passed

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† This paper embodies the results of an investigation of the Tate process of electrolytically water-proofing textile fabrics by the Committee on Science and the Arts of The Franklin Institute.

through a solution of alum, aluminium sulphate or aluminium acetate. Owing to the reaction which takes place between the soap and the aluminium salt, an aluminium soap (aluminium oleate or aluminium palmitate) is deposited on the yarns or fibres of the fabric in the form of a veneer or coating. While this veneer is fresh it is highly elastic, adhesive and water-repelling, but unfortunately these conditions subsist only for a short time. When the fabric is exposed to the drying influence of the atmosphere, deterioration is rapid, and in a few weeks the qualities of elasticity and adhesiveness disappear and the aluminium soap becomes friable, breaking away from its anchorage and thus restoring the fabric to its original absorptive condition. Furthermore, while the aluminium soap is insoluble in water, it is dissolved by gasoline, benzine and various other solvents employed in the process known as dry-cleaning. Garments water-proofed by this process cannot be dry-cleaned without partially or wholly destroying their water-repelling qualities.

The first mention of an attempt to apply electricity to the art of water-proofing textile fabrics is contained in U. S. Patent No. 558,717, issued to H. L. Brevoort in 1896. In Brevoort's process the fabric, previously moistened with water, is placed "between and in contact with an anode of an oxidizable metal and a cathode of conducting material covered with an absorbent fabric," and, owing to the physical contact between the surface of the anode and the fabric, the oxide formed at the positive electrode is deposited "on or in the fabric." Since, however, Brevoort did not provide any apparatus for applying his process on other than an experimental scale, his results are only of interest as experiments. Besides, fabrics treated by this method are but partially water-proof.

Four years later a patent¹ representing an attempt to provide a mechanism to apply the Brevoort water-proofing process to textile fabrics on an industrially operative scale was granted to J. T. van Gestel. However, in a second patent² of the same date, van Gestel abandoned his efforts to operate the Brevoort process and introduced one of his own which, in so far as the final physical results were concerned was similar to, but not identical with, the former.

The van Gestel process consists in first thoroughly impreg-

¹ U. S. Patent, No. 653,715, July 17, 1900.

² U. S. Patent, No. 653,716, July 17, 1900.

nating the fabric with a solution of a soluble metallic salt, capable of yielding an insoluble oxide on electrolysis, and then placing the wet fabric between non-oxidizable electrodes and passing an electric current through it. It is claimed that there is produced from the salt an insoluble oxide in the interstices of the fabric, whereby it is rendered water-proof. As a matter of fact the insoluble oxide would be precipitated at the surface of the cathode, and a fabric in physical contact with this surface would receive and retain a portion of this precipitate, but the penetration would be relatively shallow. Since, however, the negative electrode is surrounded with a muslin covering, it would seem that with an apparatus so arranged all the insoluble oxide would remain in the muslin and little or none of it would be in the fabric being treated. No record has been found of this process having been employed on a commercial scale.

In the Tate process of electrolytically water-proofing fibrous materials,³ not only is the fabric impregnated with a water-repelling substance, but it is claimed that the inner capillary system of the fabric is filled with this substance.

This process was first installed on an industrial and commercial basis in the autumn of 1916, in the City of Montreal, where it was operated during the war by an imperial commission; and subsequently in New York City. In July, 1920, the New York plant was transferred to Cranston, Rhode Island, where an additional equipment has been installed to provide a maximum capacity of about 30,000,000 yards per annum of electrolytically water-proofed and electrically converted fabrics.

Essentially the Tate process consists in passing the fabric, previously saturated with a solution of sodium oleate, between a graphite cathode, over which flows a solution of aluminium acetate, and an aluminium anode which is completely enveloped in a heavy woolen pad. This pad is an important and distinctive feature of the invention, and before its introduction the water-proofing was quite irregular.

The historical development of the process from the original, crude, water-proofing mechanism, consisting of the small cylindrical anode and cathode shown in Fig. 1, covers four periods represented by as many types of water-proofing machines. With the first type of machine water-proofing was effected by passing the

³This process is covered by U. S. Patent, No. 933,861, issued September 14, 1909, and by several other patents issued subsequently.

fabric between pairs of rollers. The negative roll consisted of a cylinder of acheson graphite with electric contact through a collector brush at one end, while the positive roll consisted of a metal

FIG. 1.

spider on which was spirally wrapped a one-inch square aluminium drawn bar. Inasmuch as a certain time period is required for the proper impregnation of the fabric, and since, furthermore, the rollers had a very small area of contact, the speed of this machine

had to be adjusted to permit of the necessary time interval for reaction. This limited the output on a single strand of fabric to about thirty-four inches per minute.

In the next commercial development, one of the roller electrodes was replaced by a stationary sector electrode for a length of contact of about five inches. In this machine the fabric was drawn between the one roller and the sector at a speed of about five yards per minute, and results obtained which were quite as satisfactory as those with the slower unit with two rollers.

In the third type of water-proofing machine, both rollers were

FIG. 2.

dispensed with and the material to be treated drawn between flat plate electrodes of aluminium and graphite, contact between the fabric and the electrodes being maintained by adjustable spring pressure. A battery of four of these machines is shown in Fig. 2. With this machine an output of about twenty-seven yards per minute was obtained as against an output of thirty-four inches with the first type of machine. Since in this unit no provision had been made for automatically relaxing the pressure when sewn lengths of fabric passed between the electrodes, the machine had to be stopped and the upper electrode lifted every time a seam came by, otherwise the fabric would tear. This difficulty has been overcome in the latest type of machine, a photograph of which (two units) is

FIG. 3.

shown in Fig. 3, and a diagram (one unit) in Fig. 6. In this unit the electrodes are vertical, the anode consisting of an aluminium plate (7, Fig. 6) one inch thick by eighteen inches wide and either sixty or seventy-two inches long, and the cathode of eight graphite bars (8, Fig. 6) one and one-half inches thick by two inches wide and the same length as the anode. These graphite bars are spaced one-quarter inch apart, and their ends fit loosely between metal guides which are inclined downward toward the anode (Fig. 4).

FIG. 4.

When a seam (A, Fig. 4) passes between the electrodes, each graphite bar in turn moves backward and upward and, when the seam has passed, immediately falls back to its original position. Recently a spring device (10, Fig. 6) has been installed on the vertical graphite electrodes for the purpose of permitting a delicate regulation of the pressure of each segment of the electrode on the fabric. With this device the operator can maintain a constant tension on the material being treated, regardless of its character or thickness. This regulation is very desirable and a decided improvement over the form of gravity contact, which exerted the same pressure for the finest silk or the heaviest duck. The

mechanical form of this device, shown in detail in Fig. 5, consists of a brass screw, A, threaded through a bracket, B, which is attached to each end of every graphite segment, C. The bottom end of these screws is in the form of a plunger which enters the cylinder, E, this being suitably attached to the electrode frame, F. This cylinder contains a spring, G, which is compressed by the plunger when the screw is tightened down by the small insulated knob, H.

FIG. 5.

The operation of the water-proofing process with the most recent type of machine is as follows:

Woolens are thoroughly washed with soap and rinsed in water at a temperature of about 150° F. to remove any excess of wool grease or soap that may have been left during the process of manufacture. Cottons are all destarched by a suitable process and freed from all foreign matter. In both cases this is done with the object of cleansing the fibres and opening their capillary pores for subsequent refilling with water-repelling substances.

The fabric then enters the water-proofing machine, Fig. 6, where it is saturated with an attenuated solution of sodium oleate (preferable to sodium palmitate) contained in each of the two baths, 8. From these baths it travels up over the brass idler roll, 14, and passes downward between the electrodes, 7 and 8, between which a current of from 30 to 60 amperes flows, the current density depending upon the nature of the fabric and the character of the

treatment required. The course traveled by the fabric is shown by the broken line in Fig. 6.

From troughs, 13, connected with a suitable supply system, the aluminium acetate solution is fed between each of the one-quarter

FIG. 6.

1. Frame. 2. Frame Extension. 3. Frame extension support. 4. Wash tank. 5. Solution tank. 6. Quetch frame. 7. Anode-aluminum. 8. Cathode-graphite. 9. Graphite support-side. 10. Graphite adjuster. 11. Graphite support-end. 12. Acetate trough support. 13. Acetate trough. 14. Idler roll-brass. 15. Quetch idler roll-rubber. 16. Tension rod. 17. Tension rod holder. 18. Tension rod holder bracket. 19. Frame spreader rod.

inch openings separating the graphite segments of the cathode, 8. On coming into contact with the sodium oleate contained in the fabric, the aluminium acetate reacts with it to form an insoluble

aluminium oleate which is deposited on the surface of the fabric. A thorough and even distribution of the aluminium acetate is effected by means of a number of ducts on the contact face of each graphite segment. These ducts are cut one-eighth inch half-round at an angle of 45° with about one and one-quarter inch intervals. On each alternate segment the angles are reversed. By means of this arrangement the acetate flows down with the fabric, but while the latter moves with a vertical motion, the acetate flows down in a zig-zag path, maintaining a constant, even saturation throughout the whole electrolytic period. Additional one-quarter inch half-round ducts cut vertically about one-half inch from each end of every segment drain off the surplus acetate, thus eliminating the possibility of the insulation of the electrode supports being broken down.

When the woolen pad (not shown in Fig. 6) covering the anode, 8, first goes into action it is saturated with water, but during any given period of operation no further use of water is necessary as it then works through the saturated fabric. The active aluminium hydroxide formed at the anode is taken up by the pad and distributed evenly over the surface of the fabric, and is probably carried into the interstices of the fabric owing to kataphoresis. That the aluminium hydroxide readily passes through the pad and into the fabric is due to the fact that the suspended particles of the hydroxide are positively charged and are attracted, therefore, toward the cathode. In the van Gestel process, on the other hand, the water-repelling substance formed at the cathode cannot pass through the muslin covering to the fabric, in consequence of its attraction toward this electrode.

After passing between the electrodes, 7 and 8, the fabric then travels through the bath, 4, of running water, where it is thoroughly washed; thence to squeeze rollers immediately above the bath, to a second oleate bath, and through a continuation of the process just described, except that now the electrodes and their treatments are reversed. With cotton goods, irrespective of their weight and thickness, four treatments are essential with alternately reversed action. With silks and woollens two treatments—one reversal—are sufficient. This is due to differences in the physical structure of cotton, silk and wool fibres.

When the electrolytic treatment is complete, the fabric is

washed, dried by passing between a series of steam-heated drums, and rolled or folded.

The writer has examined and tested various kinds of textile fabrics that have been water-proofed by the process described, and has found that they possess remarkable water-resisting qualities. For example, tests on the resistance to water pressure, carried out with a thin cotton that had been water-proofed for making light-weight tents, showed that whereas the untreated cotton broke down under a water pressure of one-half inch, water did not pass through the electrolytically treated material until the pressure attained twelve and one-quarter inches. Regarding the serviceability of this water-proofed tent material, the following quotation from the letter of a camper may be of interest:

I am enclosing a picture taken on my canoe trip down the Whitefish last summer that shows you just how useful the eight-foot square of light-weight tent cloth, water-proofed by the Tate process, which you lent me, proved to be.

Coming back we struck two days solid rain, and the little water-proof patch was a wonder. We used it nights as a tent and days as a cover over our duffle, and though wet all the time, it never leaked a drop. I wouldn't have believed it possible if I hadn't slept dry as a bone under it two soaking nights.

Determination of the maximum water pressure that could be sustained by a number of samples of untreated and electrolytically water-proofed duck led to the following observations: Invariably when an untreated piece of duck broke down and water flowed through, it was found that on releasing the water pressure and re-applying it, water began to leak through the duck immediately; on the other hand, with the treated material, when the pressure was released after the water first leaked through, it was found that the pressure could again be raised to the first value before leaking recommenced. Unlike the untreated duck, when the maximum water pressure is reached with the water-proofed material the water does not leak through in one or two places but in a large number. Notwithstanding the marked water-resisting qualities of the water-proofed materials, these are found to contain but 0.3 to 0.4 gram of aluminium oxide per square foot.

In order to ascertain the efficacy of the electric current in the process that has been described, two tests have been carried out with the three following samples of very heavy duck taken from the same roll: (A) *Untreated duck*; (B) *duck that had passed through the electrolytic water-proofing machine and subjected to all*

the conditions of the normal water-proofing process, except that the electric current was not flowing; (C) duck that had been subjected to the normal electrolytic water-proofing process. Test No. 1. Small seamless bags of the same shape and size were made from the samples A, B, and C. These bags were suspended and the same volume of water was added to each. The water leaked through the bottom of A at the end of one and one-half seconds; through the bottom of B at the end of thirty-one seconds; while at the end of three weeks no water had leaked through C. *Test No. 2.* Portions of the samples A, B, and C were dyed under the same conditions with a dye the action of which depended on the presence of an aluminium mordant. Sample A took up but very little of the dye; sample B was dyed a deep red, and sample C a very much deeper shade, thus indicating that while the chemically treated sample B contained aluminium compounds, the electrolytically treated sample C contained much more.

It might be supposed that the fabric would be tendered by the water-proofing process. This is not so, however, as experiments show that there is an actual increase in the strength of the fabric approximately equivalent to the increase in the filature.

A study of the electrolytic water-proofing process has led to the conclusion that the water-proofing of fabrics is due to two distinct electro-chemical operations: One, the electro-chemical formation at the anode of aluminium hydroxide which, owing to kataphoresis, is probably carried into the capillaries of the fabric; the other, the deposition on the fabric (probably only on its surface) of a film of a basic aluminium oleate resulting from the interaction of aluminium hydroxide formed electro-chemically at the cathode with the aluminium oleate produced chemically by the aluminium acetate flowing over the cathode and the sodium oleate contained in the fabric. The formation of a basic aluminium oleate, and not ordinary aluminium oleate, at the cathode, is substantiated by the fact that although both ordinary aluminium oleate and the aluminium oleate formed in the electrolytic process are insoluble in water, the former is soluble while the latter is insoluble in liquid hydrocarbons such as gasoline and benzine. Moreover, chemical analyses of the aluminium oleate scraped from the negative electrode during its formation have shown that this substance contains a considerably higher percentage of aluminium than ordinary aluminium oleate, thus proving it to be a different compound.

In addition to water-proofing, all fabrics treated by the Tate process become mildew-proof, as attested by numerous tests under conditions to which untreated fabrics invariably succumb. This feature is not attributable to any germicidal qualities of the metal salts employed, as they do not possess this property. It is due to the fact that the water-proofed fabrics receive under impact or bombardment only relatively small quantities of water, the surface penetration being very shallow, and do not, therefore, retain moisture for periods sufficiently prolonged to effect the cultivation and growth of the germ. It has been found that if treated fabrics are kept in constant contact with still water in a mildew-laden atmosphere at relatively high temperatures, they will succumb to the attack in a period of about five weeks, but this environment is rarely encountered under general service conditions. In its relation to textile fabrics of cotton manufacture, as used for tents, awnings, sails, tarpaulins and similar coverings exposed to the elements, this feature involving preservation and prolonged utility is in many instances quite as valuable as the water-repelling quality.

The influence of aluminium salts in fixing dyes is well known, and the electrolytic process, involving as it does the use of these salts, will probably fix many fugitive dyes and render them impervious to the dissolving action of water.

The electrolytic water-proofing process also performs coincidentally and thoroughly the operation of shrinking, and all fabrics thus treated are less liable to subsequent structural change of this nature through atmospheric or other action due to the influence of moisture. Microscopic examination shows that the process straightens the fibres and sets more evenly the threads or yarns of the warp and woof in fabrics wherein unevenness in this respect is present. Indeed, the changes wrought in goods of cotton manufacture bring about a complete transformation and, altogether apart from the water-repelling qualities imparted, add intrinsic value through the production of a new and better class of fabrics as judged by the recognized standards of the textile industry. This converting process does not, however, stop here. It has been found that upon calendering cotton or worsted fabrics, under ascertained conditions of temperature and pressure subsequent to water-proofing, higher surface lustres are attained than under standard finishing conditions. These lustres vary in degree from the depth

sheens usually associated only with natural silk fabrics to the brilliant surfaces which distinguish the most highly finished satins; and it is remarkable that these visual characteristics are in each instance confirmed and emphasized by the sense of touch. All of these conversions are effected without in any way impairing the water-repelling qualities originally imparted to the fabrics.

In conclusion, it will be seen that the development of the Tate process as applied to textile fabrics of all classes has advanced so far beyond the isolated achievement of rendering these materials non-absorbent, and has effected changes so entirely novel and comprehensive in their ascertained scope and potential significance, that the term water-proofing conveys a totally inadequate conception of the field which the process embraces. The electrolytic treatment represents a combined process of water-proofing and converting, while in the succeeding stage of calendering, the weave, shade, color and texture of fabrics other than woollens may be altered to predetermined degrees, producing in each instance a new and higher class of fabric, as compared with the original and as judged by recognized trade standards.

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A Photographic Seismograph.—The seismograph is an instrument for recording earthquake shocks. The instruments in general use are so constructed that a strip of paper records any vibration, and the time of any special disturbance can be noted. The principle of construction requires a delicate adjustment of levers and amplifiers of the motion. By the introduction of sensitive paper instead of the method of inking, a simpler apparatus has been obtained, which is described by Doctor Bomet in *Photo-Pratique*. A small mirror, capable of oscillating with any earth-movement, receives a beam of light and reflects it upon a strip of sensitive paper. As the reflected ray moves through an angle which is twice that of the angular motion of the mirror, the oscillations are increased two-fold in extent. The strip of paper is, of course, kept in constant and regular movement. The mechanical construction is given in detail in the article, but need not be repeated here. Electric lamps are used for illumination. From time to time the paper strip is removed and developed and gives a clear picture of the movements to which the apparatus has been subjected. It is now well-known to experts in this field that earthquake shocks often pass through places without attracting any attention from the inhabitants. It is stated that the tremendous volcanic explosion in the Indian Ocean in 1885, by which a large part of the island of Krakatoa was destroyed, produced seven successive shocks around the earth.

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