# Immunized Cotton

*By* G. TAGLIANI.

In 1924, a new product called Immunized Cotton was put on the market in Europe by the Chem. Works, formerly Sandoz, in Basel. Two years ago, the article was introduced in this country under U. S. patents by the Munitex Corporation of Paterson, New Jersey, and since then has met with ever increasing demand.

Before considering the practical use of Immunized Cotton, it may be interesting to look back at the problems which led to this invention.

Artifical fibers such as denitrated nitrocellulose and celluloses regenerated from viscose and cuprammonium solutions all show properties similar to strongly hydrated cellulose, such, for example, as an increased affinity for dyestuffs especially for direct cotton colors. On the other hand, the acetylated derivatives of cellulose differ materially in this respect since, owing to their essentially acid character, they possess no affinity for the direct cotton colors but still are capable of absorbing readily dyestuffs containing basic groups and diazotizable amine bases. Should the acetyl-cellulose, however, be subjected to partial hydrolysis, a regenerated normal cellulose can readily be obtained, though at the cost of a loss of weight and change in the appearance.

The very special dyeing properties of acetyl-cellulose have awakened the interest of chemists who had already observed similar properties in the acidic and sulphonic acid derivatives of cellulose and in oxidized cellulose, all of which show a resistance, more or less marked, towards the absorption of direct cotton colors, together with a great affinity for colors of a basic nature.

The search for a somewhat cheaper material, having no appearance of an artificial fiber has as its immediate object a treatment, applicable to loose cotton or to yarn which, without altering its physical structure, will confer upon same dyeing properties similar to those possessed by acetyl-cellulose. Such a process would undoubt-

edly be of marked importance to the textile industry as a whole; and in particular to such branches as deal with the production of cloths containing white or colored-effect threads which are cross-dyed.

Early attempts to obtain such results involved the impregnation of the goods with suitable drying oils or the precipitation on the fiber of certain higher metallic oxides. With these, however—as also with certain other proposed methods—the uncertainty of the results obtained, the fact that both fiber and dyestuff were liable to deterioration by the reagents used, and also that, viewed from a commercial aspect, the processes were uneconomic and of low efficiency, militated seriously against their adoption as a practical treatment.

The solution of this problem of obtaining two-color or white and colored effects in piece-dyeing must naturally begin by an examination from a purely chemical standpoint of the possible alterations of cellulose, and it is only by virtue of many observations and experiments carried out in this direction that a satisfactory solution has now been achieved.

As an example or preliminary experiment may be cited the slight acetylation of cotton in an acetic acid amosphere. This reaction, which appeared quite possible, had been used at an early date in Europe. This ester, however, was very unstable.

Progress was made by the conversion of cotton cellulose into its mono and dibenzoate, stearate and palmitate by which, under given conditions, the fiber structure is scarcely altered, and must be regarded as of great interest from the standpoint of the production of perfectly stable esters of high molecular weight.

The action of the carbonyl chlorides of mono aromatic acids on the sodium compound of cellulose (to which attention has been called by earlier workers) indicated a line of research which promised well, although it is well known that compounds produced by the interaction of pure sodium-cellulose and acid chlorides of aromatic acids (such as benzoyl, phthalyl, naphthoyl chlorides, etc.) are readily saponified by alkalis and cannot, therefore, be regarded as of good stability. However, by permitting the acid chlorides of aromatic sulphonic acids, i. e., sulphonic chlorides, to react under suitable conditions in presence of inert solvents with sodium cellulose, it is found that stable sulphoesters of cellulose are formed, comparable in their permanency with the original textile material from which they are derived.

The choice of a suitable sulphonic chloride for this purpose includes ortho- and paratoluene sulphonic chlorides, naphthalene sulphonic chloride and analogous bodies prepared from substituted aromatic hydrocarbons, together with chlor-, brom- and nitro- derivatives of these compounds. In practice, on the score of price, it is found desirable to use paratoluene sulphonic chloride.

It is improbable that the chemical combinations referred to can occur in absolutely quantitative fashion in an aggregate of fibers, and should an attempt be made to carry the reaction to completion, it is likely that a total destruction of the cellular structure of the cotton would ensue. This possibility must be guarded against in any technical process based on the foregoing method. The conversion of the cellulose of the fiber into hydrocellulose must take place in such a manner that esterification proceeds in successive layers. Actually, the outermost layers of the fiber are swollen by the alkali treatment, and are hence in a highly reactive condition, while the outer layers readily react with the esterifying agent, the inner layers are to a large extent protected from its action. By a suitable regulation of temperature, it is possible to bring the reaction to an end at this point.

Under these conditions, the final result of esterification may be regarded as definite and unalterable, since it is found possible to repeat the whole process of esterification on cotton already esterified without producing any further change. At present, it is not possible to give an exact and precise explanation of the mechanism of the reaction, but it is at least certain that the formation of the cellulose ester in a fiber-bundle (as yarn) and most probably in a single cotton fiber, occurs peripherally. This can be readily demonstrated by treating the esterified yarn by a suitable solution capable of dissolving cellulose, and examining the material obtained by subsequent precipitation.

Analysis of commercial Immunized Cotton shows a content of 1.9% sulphur. Assuming for cellulose a general formula $(C_6H_{10}0_5)$m., this would indicate that for nine or ten $C_6H_{10}O_5$ groups, one paratoluolsulfochloride residue is present.

From this we can readily see how it is that the structure of esterified yarn and of the single esterified cotton fiber exhibits so little physical alteration when compared

with the original material—from a technical point of view, a most important fact. We are also better able to consider what necessary precautions must be taken when dyeing such esterified cotton since we know with some accuracy the limits to which it is possible to go.

It is also obvious that, in order to get uniform results in Immunization, the cotton fiber must be free from any impurities such as fat, wax, pektin, etc. In a practical way, the cotton is cleaned by kier boiling.

The single cotton fiber, esterified by treatment with p-toluene sulphonic chloride, is altered in certain particulars as compared with untreated cotton. It is whiter in appearance, less transparent, less polished, has a lower hygroscopicity and is thickened. The lumen has shrunk or disappeared entirely, the cross section resembling that of mercerized cotton. As yarn, it possesses a fuller handle and a lower wetting-out capacity, and shows no loss of resistance, as compared with ordinary cotton, toward such operations as bleaching with chlorine compounds or treatment with cold concentrated caustic lyes, sulphuric acid or nitric acid. In consequence of these useful properties, it may be employed in figured goods which are subsequently to be mercerized, either by acid or alkaline processes, or have to be given with "Phinana" treatment. It is seen, therefore, to possess a more pronounced resistance than is found among the group of artificial fibers.

Cellulose so altered by the action of sulphonic chlorides is on the market under the name of "Immunized Cotton." This name indicates the capacity of the material to resist the dyeing action of the direct cotton colors. The immunity is dependent on the purity and degree of twist of the yarn on the one hand and on both the constitution and solubility in water of the dyestuffs on the other. Immunized yarn exhibits at least as great, if not a greater, affinity for basic colors and for certain special acid colors and gallocyanines having a basic character than do the acetyl silks. This yarn, moreover, readily absorbs from the "dyebath" diazotizable amine bases, so that its possibilities of employment are fully as interesting as those of acetyl silk—more so, perhaps since cotton, first dyed with suitable dyestuffs, can then be immunized, giving dyeings of greatly enhanced fastness when compared with similar dyeings on untreated cotton. It is clear, that for this purpose, dyestuffs have to be selected that do not contain free OH of $NG_2$ groups, since such dyestuffs would react with paratoluolsulfochloride resulting in a change or even destruction of the shade. Moreover, the conversion of cotton into Immunized Cotton can be carried out locally on either yarn or piece-goods by the aid of suitable mechanical apparatus, whereby the initial formation of sodium-cellulose is followed by esterification of the material over chosen areas. These new and purely chemical reserve effects can be employed so as to produce many and varied color contrasts, and carry the process into the wider area of color-printing. It becomes possible, in this way, to obtain white and colored reserve effects according to the choice of acid or basic and direct dyestuffs which may be applied together in the same bath. It is also possible to print white and colored discharges on the top of such effects with the production of complex multi-color prints.

In the two years during which Immunized Cotton has been on the market, new fields for its use have opened. Today it is successfully used in the hosiery trade, in dress goods, men's wear, draperies, etc., and it has more than fulfilled the expectations of its inventors.