Silk Substitutes.

Mr. Edward Lodge in a very interesting paper read before the Huddersfield Technical College Textile Society divides these substitutes into two main groups, viz:

(1.) Attempt to improve the lustre of natural fibres.

(2.) To build up or synthesise an entirely new artificial fibre.

(1.) To IMPROVE THE LUSTRE OF NATURAL FIBRES. Amongst these may be cited the suggestions of Hoseman (1881), who proposed to take advantage of the well-known property possessed by silk of dissolving in caustic alkalies and forming a solution from which the silk substance is precipitated by the addition of an acid. Hoseman's plan was to cause cotton threads to pass through a caustic—silk—solution in such a manner that they became thoroughly saturated. After wringing out excess of liquor, he passes the cotton through a diluted solution of sulphuric or phosphoric acid, which causes a precipitation of the silk substance, and thus coats the fibre with a film of silk.

Brodbeck (1890) reverses Hoseman's process by passing the cotton through diluted sulphuric or phosphoric acid, and then through a caustic-soda solution of silk. Brodbeck patented an alternative process, in which he first treats the cotton with an ammoniacal solution of copper or nickel oxide, squeezes out excess, then enters the cotton into a bath containing a solution of silk dissolved in hydrochloric, sulphuric, or phosphoric acids.

Unguad (1898) proposes to saturate the cotton fibre with a caustic-soda solution of silk waste, and to precipitate the silk substance in an insoluble form by means of carbonic-acid gas or a solution of bicarbonate of soda.

Lewis Aubert (1883) attempts the lustring of cotton (1) by a treatment with caustic soda at 18.2° Tw., from which solution the cotton is squeezed, and then (2) treated with hydrochloric acid, 9° Tw., washing, and (3) bleaching the cotton with sodium hydrochlorite; (4) treating with a bath of glucose standing at 12° Tw., and drying; (5) working the cotton in a concentrated mixture of nitric and sulphuric acids, which is said to convert the glucose into nitro-saccharose and the cotton into bi-nitro-cellulose; after rinsing, the cotton is then (6) treated with a soap solution, and finally (7) worked in a solution of tannic acid.

Later (1896) Dr. Knecht proposes to dissolve wool or silk by means of barium hydrate, precipitating the barium by means of carbon-dioxide, adding to the silk solution so obtained 10 per cent. of formaldehyde, padding the cotton goods in this material, and steaming under pressure (15 lb.) for half-an-hour, and lastly, washing.

None of these methods has received industrial application, as the degree of lustre obtained does not warrant the expense of the process. It is interesting to note that the processes of Hoseman, Brodbeck, Unguad, and Knecht result in the "animalising" of the vegetable fibres. It was hoped that these processes of depositing a coating of animal matter (wool may be used in place of silk) on the vegetable fibres would sufficiently change their nature in the direction of animal fibre as to enable the "animalised" fibre and wool or silk to be dyed and worked up together in the same way as all-wool or all-silk goods. These hopes have not been industrially realized.

The one successful method which has accomplished the modification of the cotton fibre, so as to increase lustre, is that due in the first instance to John Mercer, and perfected chiefly by Lowe, and Thomas, and Prevost. I allude to the process known as mercerising. This process is based upon the fact that when cotton is steeped in cold concentrated caustic soda the cotton fibre loses its twisted tape-like structure, becoming rounded and semi-transparent, and when immersed whilst under tension a high degree of lustre is developed, especially in the case of the long-staple Sea Island and Egyptian cottons. This process is now very largely practised, although the lustre is not equal to the lustre of the finest silk, or of some of the so-called artificial silks.

(2) Artificial silk. It is under the second class that success has been achieved in the manufacture of a fibre having lustre equal to and even surpassing the beautiful lustre of natural silk. The idea of producing an artificial fibre appears to be due to Reaumur, so far back as 1734, and to have lain forgotten for over 100 years, when Andemars, of Lausanne, in 1855 obtained letters patent for the production of artificial silk. According to Andemars' patent, he reduces the young branches of the mulberry tree to a paste, bleaches and purifies the paste, and finally transforms it into an explosive substance (probably nitro-cellulose), which he dissolves in a mixture of alcohol and ether, and to which he adds some rubber solution. The thread was then spun from the viscous fluid by means of a simple point of steel, which was dipped into the mixture and then drawn out. The point drew the viscous thread, which rapidly dried, and was at once wound on to a bobbin. The idea did not prove practicable on any scale. The search for a suitable filament for the electric incandescent lamp led Sir William Crooks, Weston, Swan, Swinburne, and Wynne and Powell to experiment on lines laid down by Andemars. They conceived the possibility of manufacturing an artificial filament for incandescent lamps from a body known as cellulose-nitrate impregnated with rare earths. The researches of these investigators prepared the way for the more successful work of Count H. de Chardonnet (1885).

According to published accounts, Chardonnet finds the most suitable strength of acid to be a mixture of 15 parts of nitric acid 1.52 sp. gr., and 85 parts of sulphuric acid 1.84 sp. gr. He steeps one part of cellulose in nine parts of this mixture for about six hours; the cotton is then freed from excess of acid, thoroughly washed with water, and finally subjected to hydraulic pressure. The pyroxyline so formed is pressed to such a degree that 36 per cent. of moisture is left in the mass. At this stage it is introduced into a slowly revolving horizontal tin-lined drum, in which it is treated with a mixture of equal parts of 95 per cent. alcohol and ether, 100 parts of this mixture to 22 parts of cellulose nitrate. The solution is complete in 15 to 20 hours. The liquid so obtained is filtered through cotton wool, a pressure of 30 to 60 atmospheres being necessary for this purpose. Lehner has since shown that the addition of a small per cent. of H_2SO_4 causes the viscous fluid to flow under much less pressure. After storing for some time it is introduced into the spinning apparatus, which consists of a stout reservoir, from which the viscous fluid is forced, by continuous air pressure, through a vertical tube, terminating in a glass or platinum nozzle with an opening 0.1 to 0.2mm. in diameter, and an edge not thicker than 0.1mm. The viscous thread produced is immediately dried in a current of air at a temperature of 45° C., or coagulated by water or a 0.5 per cent. solution of nitric acid. The artificial fibre is then successively treated with solutions of Na_2CO_3, bisulphite of soda, albumen, phenol, or a salt of alumina or mercury. Dry spinning is now said to be the rule, the solvent rapidly evaporating as soon as the fibre reaches the air. Several fibres are spun together to form a thread. At this stage the threads are very inflammable, and even explosive; they have therefore to be denitrated. This is accomplished by passing through ammonium sulphide or some other reducing agent, which removes the nitric oxide radicles and substitutes hydrogen, thus regenerating the original cellulose, which is not more inflammable than ordinary cotton.

The cost of this product is said to be not more than 50 per cent. that of natural silk. Its tensile strength is variously stated at from 50 to 80 per cent. of boiled china-silk. It absorbs about 16 per cent. of moisture as compared with natural silk 11 per cent. Chardonnet silk is grey-white, possesses a high degree of lustre, is less soft to the handle than silk, and is without "scroop."

The diameter of thread varies from 0.001 to 0.04mm. Under the microscope it appears as a thread of irregular thickness, generally a little flattened, and resembles Tussah silk in the presence of longitudinal striation.

Lehner's Silk (1900) is manufactured by a process similar to Chardonnet's. He, however, uses as his solvent for the cellulose nitrate a mixture of methyl alcohol, ether and ethyl sulphate; the strength of the solution being equal to 8 per cent. of cellulose nitrate. In one of his patents he claims the use of a mixture of five parts of cellulose nitrate and one part of silk substance, which he obtains from silk waste by dissolving in ammonium copper oxide, and afterwards neutralises and precipitates with acids, washing with water and re-dissolving in concentrated acetic acid. The spinning is carried out by causing the fluid to flow through fine orifices into water, turpentine, petroleum, carbon, disulphide, or chloroform, which cause the fibre substance to congeal to an insoluble fibre. Denitration of the fibre is carried out by treatment with a diluted solution of nitrate of soda. In lustre it is equal to Chardonnet's. In strength, elasticity, and color it closely approximates to Chardonnet silk.

Du Viviers Silk (1888) claims the use of three solutions:—(1.) 7 per cent. solution of tri-cellulose nitrate dissolved in glacial acetic acid (eight parts). (2.) 12.5 per cent. solution of gutta-percha dissolved in carbon di-sulphide (one part). (3.) 5 per cent. solution of isinglass in glacial acetic acid (two parts). These bodies are well kneaded together with the further addition of small quantities of glycerine and castor oil. The spinning is carried out in an apparatus similar to that employed by other makers, being delivered into a solution of caustic soda, and after washing in water, passed through dilute acetic acid. The threads are then successively treated with albumen, mercury chloride, and CO_2 gas. The fibre is brittle, but beautifully white.

Many years ago John Mercer discovered that cellulose would dissolve in a strong solution of copper oxide in ammonia (cuprammonium), forming an extremely viscous fluid, which, when allowed to dry in thin layers, produced an insoluble film of considerable tenacity. It is colored green owing to the presence of copper. This observation has proved to be of great technical importance, notably in the production of the "Willesden paper," and for waterproofing canvas for tents and sails, pickling cordage, etc.

When this substance is treated with an acid, the cellulose is set free in a pure white condition, the acid binding the copper. After many attempts by several investigators, Pauly (1897) and others have succeeded in producing one of the most perfect of artificial fibres, which has been put on the market under the name of "Glanzstoff."

The solution of copper can be prepared in several ways. For example: Copper turnings are treated with ammonia in presence of lactic acid at a temperature of 4 to 6° C. At the end of about ten days the intense blue solution of copper oxide is sufficiently concentrated for use.

Preparation of the cellulose solution: 100 parts of cellulose are mixed with 1000 parts of a solution containing 30 parts of sodium carbonate and 50 parts of caustic soda, and warmed in a closed vessel for 3½ hours under a pressure of about 2½ atmospheres. The mercerised cellulose thus obtained is washed, dried, and bleached by chloride of lime, and again washed and dried. Seven to eight parts are now mixed in a machine with the copper solution. The cellulose slowly dissolves, the end reaction being determined when 4 to 5cc. run from a flask form a continuous thread. The spinning is done through capillary tubes, 0.2mm. in diameter, a pressure of 2 to 4 atmospheres being required to force it through the orifices. The viscous fluid is coagulated by passing through a bath containing 30 to 65 per cent. of sulphuric acid. The threads are then well washed and soaped.

As regards lustre, tenacity, and elasticity, this fibre is equal to Chardonnet's fibre; it also possesses the lustre of genuine silk. This process would indicate that the silk would be cheaper than Chardonnet or Lehner's silk. Pauly's silk is more uniform in structure than Chardonnet silk. As compared with genuine silk, the strength is: Silk, 100; Pauly silk, 56.

Viscose (1892); *Stearn Fibre* (1898).—These splendid examples of artificial fibre owe their origin to a most important and interesting discovery by Messrs. Cross, Bevan and Beadle. They found that when cellulose is treated with (1) a concentrated solution of caustic soda, and whilst still saturated with the soda (2) treated with carbon disulphide, and after some time with (3) water, a compound is formed soluble in water to an extremely viscous fluid, a substance which has received many technical applications, under the name of "Viscose." Messrs. Cross, Bevan and Beadle and Dr. Stearn have succeeded in producing from "Viscose" one of the best and cheapest synthetic fibres. Viscose is of an unstable character, decomposing either spontaneously on standing or heating, or on treatment with ammonia salts, acids, or metallic salts. The decomposition results in the regeneration of the original constituents—that is, carbon disulphide, caustic soda, and cellulose, the latter when in the form of film or filament being left in a highly lustrous condition.

Cross, Bevan and Beadle obtained their alkali-cellulose by impregnating cotton with 15 per cent. of caustic soda containing 12 per cent. Na_2O, and pressing until it contains 40 to 50 per cent. of its weight of soda. This is then treated with 30 to 40 per cent. of carbon disulphide in a closed vessel and with constant stirring for five or six hours, and finally adding water. The "Viscose" is purified to free it from brown substances, which would, if allowed to remain, spoil the color of the fibres manufactured from it. After a purification, the "Viscose" is forced by air pressure through fine capillary orifices into solutions of ammonium chloride or dilute sulphuric acid to coagulate the fibre.

Cellestron Silk.—Artificial fibre from celluloseacetate. If cellulose be treated for 24 hours with sulphuric acid at 103° Tw. strength, then freed from acid by thorough washing, it is found to be very tender, and breaks on rubbing. This modification of cellulose is called hydrocellulose. When this product is treated with a mixture of acetic anhydride and conc. H_2SO_4, and at a temperature between 45° and 70° C., some of the hydrogens of the cellulose are replaced by the acetyl group. This compound is very viscous, and when spun in a similar manner to that adopted for other artificial fibres, a fibre of remarkable brilliancy is obtained. The threads obtained in this way have this advantage over the other fibre, that they are not inflammable. The silk cannot be readily dyed, but can be colored by adding the color to the pulp before spinning. This silk is much used in America for covering electric wires, and is known as cellestron silk.

Fibres can be obtained by dissolving cellulose in zinc chloride. The threads are, however, weak. This fibre is principally employed for the manufacture of filaments for electric lamps.

Silk-like fibres have been obtained by the Vereinigte Kunstseid-fabriken, of Frankfurt, by spinning a solution of acid cellulose in caustic soda, and precipitating the thread as it comes from the capillaries by means of an acid. The cellulose is first treated with sulphuric acid, sp. gr. 1.55 (10 cellulose, 100 acid), thrown into water, well washed to free it from acid, and then dissolved in caustic soda (100 parts) density 11.2.

Vanduara Silk (Millar, 1899).—This fibre was introduced by A. Millar, of Glasgow, and is produced from gelatine. He describes his process as follows: 4 lb. of the best gelatine is broken up into granular pieces, such as will pass through a riddle, 16 meshes to the square inch. This is added to the melting pot with 2 lb. of pure cold water, well stirred, covered over, and allowed to stand one hour. The vessel is next placed in hot water, temperature 120° F., for another hour, stirring once or twice. At the end of the second hour a solution of gelatine of uniform consistency, and containing 66 per cent. of gelatine, is obtained. The solution is now drawn into fine filaments. The apparatus consists of a brass cylinder enclosed by a hot-water jacket. The cylinder is furnished with a series of nipples or nozzles. The upper end of the cylinder is closed with an air-tight cover. After the solution has been poured into it, the gelatine exudes from the nipples of thin thread-like streams, and these are received on traveling bands of considerable length. The filaments are very thin, and dry in less than 30 seconds. They are taken off the bands and reeled on to a bobbin before the band has made its complete circuit. The group of filaments are next twisted together and spread out in a thin layer on an open reel, about one foot in diameter. These are now placed in a chamber in which a small quantity of formaldehyde has been poured, and is therefore filled with formaldehyde vapor. An exposure to the vapor, at the ordinary temperature, completely changes the character of the gelatine. It is no longer soluble in water nor any ordinary solvent. The fibre so prepared has a splendid lustre. To obtain colored yarn, the color is mixed with the water before adding to the gelatine.

The nozzles have a bore of $\frac{1}{100}$ in., but the filament drawn from these can be $\frac{1}{100}$ in., the thickness being determined by the speed of the traveling band. Air pressure is used to force the liquid out of the nozzles. This silk is very lustrous, but of low tensile strength.

Attempts have been made to produce silk by using bichromate to render insoluble gelatine in place of formaldehyde.

Up to about a year ago artificial silks were not of sufficient strength and elasticity to stand weaving in the warp form. Dr. Thiele (Belgium) has, however, succeeded in producing a fibre which is said to be of equal elasticity to natural silk, and a strength equal to 80 per cent. that of the natural fibre, also of equal softness and covering power.

Artificial silks dye more readily than ordinary cellulose fibres; the temperature of the dye-bath should not be higher than 140° F.; for Chardonnet silks not higher than 90 to 100° F.