Dyeing of Synthetic Polymer Fibres

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DURING the present phase of intense scientific activity throughout the world, hardly a year passes without announcement of new discoveries in the fibre field. With the advent of new synthetic fibres, new problems are met with in the dyeing and finishing of these fibres. The problems which the new fibres present to the dyer and the colourist are manifold and at present seem insurmountable. In producing these fibres, the manufacturers have selected polymers that promised most in strength, abrasion and weather resistance and all-round serviceability. They have not been concerned with ease of dyeing. There are some fibres which are almost completely undyeable.

As a result of patient and extensive researches carried out, it has been possible to overcome many of the problems involved. Existing dyeing processes have been modified with the result that a wide range of shades of adequate fastness can be obtained, on most of the newer textile fibres. It is interesting to note that it has not been found necessary to create new dyes for these new fibres. Existing dyes, chiefly those used for acetate rayon and wool are found suitable for the newer fibres but with modified techniques.

Among the synthetic fibre polymers, there are six main classes :

1.	Polyamide	Nylons and Perlons L. & T.
2.	Polyester	Terylene and Dacron.
3.	Polyacrylonitrile	Orlon, Dynel and Acrilan.
4.	Polyvinyl chloride	Rhovyl, Thermovyl and Fibravyl.
5.	Polyvinylidene chloride	Saran and Velon.
6.	Vinyl Resins	Vinyons.

This list does not represent the limit of achievements, since theoretically there is no end in sight to the number of such polymers that can be synthesised. Among these, fibres of commercial importance are, Polyamides, Polyesters and Polyacrylonitriles. The remaining fibres are utilised for some special purposes. The aim of the present article is to express the dyeing technique of these newer fibres in a collective form.

Nylons and Perlons :—

The British and most American nylon and perlon T are made from hexamethylenediamine and adipic acid, while perlon L is derived from caprolactum. The methods of dyeing nylon are somewhat similar to those used for other fibres. Nylon has affinity for a wider range of dyestuffs than have other common fibres but it does not absorb the dyes very well. In general, the dyed fabrics lack in fastness to sunlight and to washing. Direct, Acid, Acetate and other classes of dyes dye nylon, although receptivity for direct, acid and vat dyes is rather low.' However during dyeing nylon fabric should either be held smooth or else be "set" before dyeing in order to prevent wrinkle formation which would be quite difficult to remove later.

The dyeing behaviour of nylon to dispersed acetate rayon dyes resembles that of acetate rayon. This class, in view of its excellent levelling properties, compatibility in admivture and ability of cover yarn irregularities, will continue to be the most popular class of dyes for

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nylon. Soluble acetate rayon dyes behave quite differently on nylon than they do on acetate rayon. The light fastness of the acetate dyes on nylon is satisfactory for such uses as hosiery. Where the best possible light fastness is desired, neutral dyeing acid colours may be preferred. Here too much of acidity and too high temperatures should be avoided. In general, acid dyes possess better fastness to washing and non-shrink finishing. An interesting feature is that the acid dyes on nylon are unaffected by stripping agents and are little affected by chlorine used in normal bleaching processes. Basic dyes possess excellent affinity for nylon but only under alkaline conditions. Unfortunately, they have very low resistance to light on nylon and their practical outlets are thus very restricted. However, they find some use on nylon for fluorescent effects. Direct dyes are also capable of dyeing nylon and maximum colour value is realised only if acid is added to the dyebath. More complex direct dyes, however, are incapable of dyeing nylon, for they only tint the fibre and hence their importance lies in the ability of certain members to leave nylon undyed. Chrome dyes cannot be applied on nylon with the usual wool technique, since nylon does not reduce the dichromate ions as wool does. This difficulty is overcome by using reducing agents. Azoic combinations cannot be applied to nylon by the normal technique employed for their application to cellulosic fibres. The aromatic bases and naphthol bodies are readily absorbed from their dispersions provided high temperatures are employed. Subsequent treatment in an acid nitrite bath effects diazotisation and coupling *in situ*. Vat dyes are also applied from alkaline solution by high-temperature dyeing as the alkaline leuco anions possess slow diffusion rates into nylon at normal dyeing and vatting temperatures. Vat dyeing on tannic-acid-treated nylon, although not so fast to light and washing as on cotton, are faster on nylon than other classes of dyes.

Sutton has obtained excellent colour yields when nylon materials are pretreated with swelling agents like cresol-sulphonic acid, phenolsulphonic acid, salicylic acid and cinnamic acid. These agents swell the fibre, and the nylon treated with them can be dyed with solubilized acetate, acid, vat and azoic dyes giving better fastness properties. During the past two years new dyes designed particularly for nylon have been introduced. These are known as " Caprocyl " dyes and have outstanding light fastness on nylon.

Perlon, the German equivalent of nylon, has the same dyeing properties as nylon ; cibacet, celliton and celliton fast dyes are most convenient, giving good penetration. The fastness to washing of the dyes is inferior on perlon to that on nylon while there is little difference in light fastness.

Terylene and Dacron :—

Terylene is a polymeric ester obtained by condensation of terephthalic acid and ethylene glycol. Dacron is a condensation polymer made by reacting ethylene glycol with the dimethyl ester of terephthalic acid. The dyeing properties of both these fibres are identical.

Terylene is similar in certain respects to both wool and acetate rayon. It is receptive towards many dyes that are free from water-solubilising groups, particularly sulphonic acid groups. Thus dyes applicable to terylene are (1) Duranols, dispersol cibacets, (2) Solacets and (3) Ionamines, of which (1) are the most important. The solacets possess less substantivity and are not salt-sensitive as they are on acetate rayon, and not acid-sensitive as they are on nylon. Ionamines offer little advantage over them with respect to the ease of dyeing, but are inferior in fastness properties to cibacets. Some improvements in the depth of shade is obtained by prolonging the dyeing period. Also it has been the practice of the dyer to add agents like s-trichloroaniline, *m*-cresol and β-naphthyl methyl ether, to the dyebath to produce the desired effect, whether it is to induce levelling, increase penetration, promote wetting, increase exhaustion or confer good handling, and the principle is well established.

Azoic dyes did not give deep shades on terylene by normal methods and so the process needed modification. High molecular naphthols did not give good results and so α-naphthol, β-naphthol, and like substances were tried and good results were achieved. The methods of dyeing terylene are similar to those employed for nylon. It was necessary however, to carry out diazotisation in hot. Vat colours dye terylene under pressure at high temperatures. Many types of dyes are also applicable by the "Thermosol dyeing process." With basic dyes terylene behaves similar to wool, but it is generally necessary to have a swelling agent present in the dyebath. But none of the water soluble dyes, including acid, chrome and direct dyes, have affinity for this fibre. Considerable progress is now being made in establishing dyeing processes for terylene. The position of this new synthetic fibre in relation to ordinary dyeing methods and dyes is very similar to that occupied by acetate rayon around 1920, when it was first introduced.

Orlons :—

These are polyacrylonitrile fibres of high resistance to acids, sunlight and high temperatures. It has very low water uptake, being even inferior to terylene in this regard and therefore is very difficult to dye. There are at present two types of Orlon (a) Orlon 81 and (b) Orlon 41. The dyeing properties of both these fibres differ to a large extent and the results obtained on orlon 41 cannot be reproduced on type 81. The dyes which can be applied to orlon under different conditions of temperature and pressure are cibacet, vat,, basic, acid, direct and chrome dyes. Acid dyes have been found to give most satisfactory results when applied by special processes.

Vat dyes have been successfully employed on orlon from a normal hydrosulphite vat, using β-naphthol as swelling agent and depth of colour is improved if pressure is increased. Certain varieties of orlon can be dyed with azoics in the normal manner. The basic dyes can be applied to orlon in presence of swelling agents like anthranilic acid. These have moderate depth of shade but poor light fastness. Acid dyes have practically no affinity for orlon without a swelling agent, but using cupric salts and hydroxyl amine as swelling agents, satisfactory dyeing takes place. The resultant shades differ from those obtained on wool and so does the fastness. The inherent difficulties in the cupric ion method have of late been overcome by the modified method and is referred to as "DRIP METHOD" or "Controlled addition of Cu method" which is discussed under dynel.

Dynel :—

Dynel is a copolymer of vinyl chloride and acrylonitrile. The fibre is dyed with a range of colours such as selected acetate dyes. Civacet dyes are applied by normal method as the migration of the dye is not so well as on acetate rayon or nylon. Since dynel will blush in boiling water or at 95°C, steps must be taken to avoid this by adding sodium sulphate, which has an excellent effect of minimising blushing. The fastness to washing of these dyes is very much better than on acetate rayon or nylon but light fastness tends to be somewhat lower. Therefore, selected acid dyes are made use of which better light fastness is required and for this a special technique is necessary. Dynel is pre-swollen with β-phenyl phenol and acetic acid is added which disperses the phenol and then cupric acetate or sulphate and hydrosulphite are added. Dynel looses some of its lustre during dyeing and relustring is carried out by heat treatment for 15-20 minutes at 120°C. Temperatures above 120°C should be avoided, otherwise shrinkage takes place. Also, mixtures of acid and acetate dyes on dynel have proved to be yielding good results.

Recently, the Textile Fibre Department of the Union Carbide and Carbon Chemical Co., has announced what is called "The Controlled addition of copper technique" for dyeing dynel and other acrylic fibres. Here a mixed solution of $CuSO_4$ and a reducing agent is added at a controlled rate to the boiling dyebath. In this way soluble, active, cuprous copper can be introduced into the dyebath at its point of maximum effectiveness. Other advantages of this method are that the amount of reduced copper is usually less than required formerly, colour values are increased and this process lends itself to exceptionally nice control.

Acrilan :—

Acrilan is the newest member of the acrylic fibre family. Its composition has not been made known ; it is believed to be a co-polymer with acrylonitrile as the predominant monomer. Acid dyes at low bath pH values in presence of nitric acid give good results on acrilan (Woodruff 1951). Actual recommendation on the best procedures for dyeing acrilan has not been made public, but very good success has been attained in applying acid to acrilan by "controlled addition of copper method" as employed for dynel.

Rhovyl, Fibravyl and Thermovyl :—

These are 100% polyvinyl chlorides and differ from dynel. The dyeing of Rhovyl, etc. is complicated by the low temperature (70°C) at which high plasticity and shrinkage occur. The dyeing of this material has been outlined by *A. M. Baron* using dispersed acetate dyes.

Suran and Velon :—

These fibres are formed by copolymerising vinylidene chloride and vinyl chloride. They can be given a wide range of attractive colours by incorporating pigments in the spinning mass. Because of the impervious nature of the material, they do not take dyes by the normal dyeing methods. However, the use of certain acetate rayon dyes has shown good results. Researches are being continued to find better methods of dyeing these fibres.

Vinyon :—

This is a copolymer of vinyl chloride and vinyl acetate. Vinyon lacks in affinity for most of the dyes. However, it can be dyed with basic dyes but the fastness to light, rubbing and washing is very poor. Acid and direct dyes may be applied to vinyon from a solvent like cellosolve. Acetate rayon dyes, also, have been found to give very good results. Recently, it is found that a type of azo has good affinity for vinyon (B.P. 568037). The dyeing of vinyon, however, must be considered as being in the experimental stage.

High Temperature Dyeing of New Fibres :—

Reference has been made to some of the difficulties involved in dyeing the new synthetic fibres, mainly due to their low water uptake. Therefore, a considerable amount of attention has been given to dyeing these fibres at temperatures above boil and it has been found that increased adsorption and penetration of dyes take place. The limitations of this technique would include the break-down of some dyes, the necessity for use of special and expensive apparatus and difficulties in matching to pattern.

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Life on American University Campus

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IT was early spring when I first arrived on a mid-western American campus. The weather was still chilly, the trees were regaining foliage and the green grass was just growing on the big spacious lawns. The first impression of the campus life was quite exciting. Hundreds of boys—tall and husky and wearing those typical zipper-jackets—and girls—smart and good-looking and covered with bright coloured spring coats were moving hurriedly, with big bundles of books in their hands, from Department to Department at the end of every hour. I still remember some of the remarks which I could overhear while I was taking a stroll on the College campus. "No Bob I can't very well make it. I have a test tomorrow", or "Jee wizz Sallie ! for heaven's sake how can I go out with Dick this evening ? I have got to finish my home-paper tonight." I was wondering why these college kids were worrying so much about their studies at the beginning of the term. In India I was used to a habit of dusting off the books at the end of December and start preparing for examinations coming two or three months after. As I started my graduate work, I soon realized that the entire American system of education is quite different than one I had been used to in India.

I soon learnt that this mid-western campus is a self-contained University town. On this campus there are different Departments or Colleges such as, Chemical Engineering, Chemistry, Physics, Mathematics, Botany, Zoology, Agriculture, Bacteriology, Metallurgy, Engineering, Home-economics, Statistics, Architecture, Journalism, Music, etc., most of them of scientific subjects as this University is for science and mechanic arts. There are also dormitories (Hostels), fraternities and sororities (these are residential clubs for boys and girls, respectively, organized on membership

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