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Some Aspects of Research in Vet Dyes

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THE discovery of indanthrone by Bohn in 1901 opened up the important field of anthraquinone vat dyes. Since then dyes of this class[1] have been synthesised in large number and they now constitute the outstanding group of all dyes because of their excellent tinctorial and fastness properties. Among the synthetic dyes the anthraquinone vat dyes are the largest consumed next to the azo dyes and on value basis, they probably surpass the azo dyes even. Being particularly suitable for dyeing cotton and regenerated cellulose (which constitute about 70% of the textiles used)[1] they have assumed a great commercial importance in spite of their high cost.

Some limitations of vat dyes and need for new vat dyes :—

The general excellence in all respects, of the present range of vat dyes may give the impression that there is little scope for further improvement or extension of the range now available. A close examination, however, reveals that although the first member of the series was marketed more than fifty years ago, there are still no bright scarlet, bright red, greenish yellow and turquoise blue dyes among them, which possess fastness comparable to the best dyes of this class[2]. Also, certain dyes, particularly yellows and oranges (e.g. Indanthrene Yellow GK and Indanthrene Golden Orange G) which are otherwise satisfactory have the drawback of tendering cellulose dyed with them, on prolonged exposure to light[3]. The need for the extension of the present range and the discovery of yellow and orange vat dyes which do not suffer from the tendering activity is therefore obvious.

Although the vat dyes owe their supremacy over other dyes to their high fastness, it should be realised that the conception of fastness is subject to continual change. New fastness requirements arise which were previously unknown. An example of this is provided by the fastness to new finishing processes[2] based on the synthetic resins such as anti-crease, anti-shrink, nonfelting and flame-proof finishes. The range of dyes which suit these developments needs further extension.

The above instance is but one among the many new problems created for the dye chemist as a result of advances made in the field of textiles. Another example is the advent of synthetic fibres such as Nylon, Acrilon, Orlon, Dynel, Saran and Terylene. Viscose rayon being similar to natural cotton gave no

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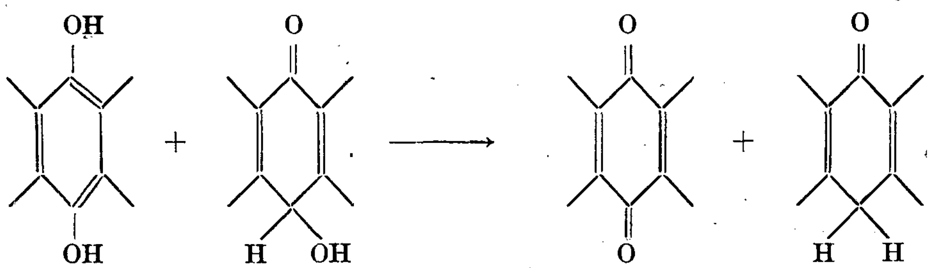
new dye problems. Acetate rayon on the other hand presented difficult problems in the initial stages but these were soon overcome to a great extent by the development of a new disperse class of dyes. Nevertheless, there is still a lack of dyes of high fastness to light and washing which will dye this fibre. The premetallised dyes found application to nylon. However, satisfactory dyes which are suitable for application to fully synthetic fibres have yet to be developed. The hardwearing properties of these fibres demand new dyes possessing high standard of fastness. The special advantage of some of these fibres is resistance to chemicals and this very resiststance is responsible for the lack of chemical affinity between the existing dyes and fibres[2]. Attempts have been directed towards the application of anthraquinone vat dyes to the new fibres in view of their high standard of fastness[3]. A partial solution of this problem was found in the use of protective colloids[3] to minimise the detrimental effects of caustic soda on alkali-susceptible fibre. Sodium hydroxide has been replaced by milder leuco-solubilising agents such as trisodium phosphate and triethanolamine. However, vat dyes applied on nylon gave shades of poor fastness. The task of finding dyes for new fibres is therefore complicated. Although the use of disperse class of dyes and the fixation of pigments on the surface of the fibres by means of synthetic resins solve some of the difficulties in the dyeing of new synthetic fibres, attempts may be made to produce vat dyes which are suitable for dyeing these fibres.

The development of new continuous methods of machine dyeing has added to the problems facing the dye specialist. The prime object of these methods being speeding up of production, vat dyes are required which can be vatted and fixed rapidly at high temperatures. Efforts in the way of simplification of the vat dyeing process led to the discovery of the solubilised vat dyes (Indigosols). The problem of securing high penetration and level dyeing has been approached from several angles and the principal remedies found are the pigment padding process (application of a non-substantive dispersion of a vat dye to the textile fibre followed by reduction-oxidation *in situ*) and the "vat-acid" process. However, the application of vat dyes is still a "lengthy, intricate and an expensive" step[4] as against the users' desire for simple methods of application. Many vat dyes can profitably be improved in fastness properties. The high money value of the vat dyes also provides an incentive for making known dyes by improved and cheaper methods.

Need for research on theoretical aspects :—

Apart from the above lines on which progress may be made, continued advances in the field of dyes is broadly related to fundamental researches in allied fields. A few chemical problems discussed below will indicate the existing need for a better understanding of the various processes in the light of the advances made in theoretical organic chemistry.

In the application of vat dyes in machine dyeing by impregnation of the fabric in aqueous alkaline hydrosulphite at elevated temperatures complications arise because of over-reduction of the dyes. In the "vat-acid" process the dye is precipitated as the hydroquinone derivative (vat-acid) by acidification of the alkaline hydrosulphite vat. The vat-acid exists in two tautameric forms, the dihydroxy and the oxanthrone form. In certain dyes the equilibrium is shifted towards the oxanthrone form. The formation of the latter is undesirable since it is resistant to air-oxidation. Further the oxanthrone is reduced by the leuco-compound present, to the substituted anthrone as shown below. It is not possible to regenerate the dye



Vat-acid Oxanthrone Dye Anthrone

by aeration of anthrone derivative.

Oxanthrone and anthrone arising out of over-reduction during the vatting process affect the shades as well as economy of the dyeing process and their formation is more pronounced in the machine dyeing where high temperatures are employed. The vatting process may thus become complicated under inappropriate conditions and there is therefore need to study the chemistry of these compounds, *e.g.* the influence of substitution on the equilibrium between leuco and oxanthrone derivatives is worthwhile investigating.

The study of the chemistry of anthraquinone derivatives presents special difficulties. Due to their high molecular weights, polycyclic nature and absence of solubilising groups the vat dyes are not readily amenable to chemical studies. Thus, they are sparingly soluble in low-boiling solvents such as benzene and alcohol and even in high-boiling solvents they dissolve only to a small extent. This lack of solubility introduces practical difficulties in carrying out reactions and investigation of the products since frequently the usual methods of fractional crystallisation cannot be employed for separation of mixture of reaction products. Coffey[4] has recently emphasised that " difficulty of the isolation, separation and identification and characterisation of individual compounds is undoubtedly one of, if not the major problem in anthraquinone chemistry........... It is the reason also why so little is to be found in the literature on the quantitative aspect of such a fundamental problem as the course of substitution reactions in anthraquinone." On account of these practical difficulties, knowledge regarding the constitution of certain vat dyes is still incomplete. Examples for this are the constitution of sulphurised vat dyes, notably Hydron Blue and Cibanone Orange R; anthrimidecarbazoles such as Indanthrene Khaki GG (The precise constitution of many dyes of this series is unknown); Indanthrene Navy Blue G, etc. Use of modern experimental techniques such as chromatography, study of absorption spectra and the fine structure of vat dyes are possible gateways to further progress in the field of vat dyes.

There is considerable research activity in the study of theoretical aspects such as relation between chemical constitution and colour, dyeing and fastness properties. These studies have been largely confined to the soluble and insoluble azo dyes, cyanine and certain basic dyes. In vat dyes however, there has not been a systematic study of the relation between chemical constitution and substantivity. This requires a collection of large amount of experimental data.

The problem of photochemical tendering activity[5] of certain vat dyes is also receiving great attention but as yet no general rules of tendering based on the chemical constitution of the dyes have been arrived at. Solution of this problem is difficult since in addition to non-tendering, other considerations such as brightness, affinity and fastness have to be taken into account.

In the face of several problems regarding the existing dyes which are still unsolved one may doubt the wisdom of the search for new dyes. However, some of the shortcomings of the group of vat dyes indicated in this article will justify continued researches in the way of making new and better dyes to suit different requirements. Fresh impetus has been given to research in chemistry of dyes by the availability of the newly discovered raw materials from coal-tar and petroleum industry such as the polycyclic compounds—pyrene, fluoranthrene, chrysene, etc. and thiophene (synthesised from butadiene). The use of these products may lead to the discovery of cheaper and useful vat dyes. In fact, there has been considerable activity in search for new vat and other dyes mostly confined to the industrial laboratories but the results of such investigations are given little publicity. However, research on technical aspects in the field of dyestuffs should go hand in hand with research on fundamental theoretical problems. For this reason, research in chemistry of dyes should be given its due importance in the university research laboratories also.

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Radiation—Processing of Foods

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IT is well-known that conventional means of heat processing irreversibly alter the flavour, colour and texture of many foods. Much research has been conducted in recent years to ascertain whether it is possible to minimise such adverse effects of heat processing. There is promise in the methods that involve utilisation of several of the radiations of the electromagnetic spectrum. Progress in this field has been substantial during the last decade partly because of the development of new equipment by physicists and electrical engineers.

What all this may mean to food industries today, cannot yet be stated fully. Canned foods may be expected to be remarkably improved, since overcooking that results from the heat processing needed to destroy spoilage organisms will be obviated. They probably would be cooked to a degree determined by palatability considerations. Other food items having relatively short periods of acceptable quality may have them extended. In addition, vast uncharted fields for the application of these radiations are daily being opened by developments in widely varying types of food processing.

Types of Radiations and Their Uses :—

All electromagnetic radiations consist of electric and magnetic vibrations of high frequency. Depending on differences

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