

chemical control is therefore unnecessary when chlorite is used as a bleaching agent. The whiteness obtained with chlorite is more permanent because the goods in this case are free from oxycellulose.

The aim of the most modern bleachers is to evolve an ideal bleaching process, viz., a single-bath process. From this point of view chlorite seems to afford a good scope for the development of such a process.

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## Luminescence, Luminescent Dyes and Pigments

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THE glowing of phosphorus in the dark is known as "phosphorescence." This phenomenon is due to absorption of radiation in daylight by phosphorus whereby the energy content of an electron is raised above its ground level. The activated electron continues to emit radiation and lose its energy content until the ground level is reached. Since the activated electron has stability over a prolonged period, phosphorescence continues in the absence of irradiation. Indeed, substances are known where phosphorescence lasts a few years. In contrast to the above phenomenon is "fluorescence" where the emission of radiation lasts as long as it is irradiated. Fluorescence ceases as soon as the source of irradiation is cut off.<sup>1</sup> Unlike in phosphorescence, in fluorescence the activated electron is unstable. Both these phenomena are covered by the term "luminescence."<sup>2</sup> The two phenomena have, however, little in common. Thus photo-conductivity—the increase in electrical conductivity under irradiation—is negligible

in fluorescence whereas it is considerable in phosphorescence. In addition, the two phenomena display differences in spectral distribution. There are seven types of luminescence which are described below :—

1. *Chemi-luminescence* is luminescence which is associated with chemical changes taking place in a substance, as in the slow oxidation of phosphorus in storage.
2. *Crystallo-luminescence*: A few substances like potassium sulphate possess the property of exhibiting luminescence during their crystallization.
3. *Tribo-luminescence* is produced when crystals of certain substances are crushed, for instance the luminescence displayed by crystals of sugar when rubbed in the dark.
4. *Cathodo-luminescence* is produced by the platinocyanides of barium, magnesium, lithium or sodium when bombarded by the cathode rays.

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5. *Incandescence* is a term applied to the luminescence exhibited by certain substances like lime when heated in an oxyhydrogen flame.
6. *Photo-luminescence* is luminescence apparent even in daylight, like that shown by zinc sulphide at room-temperature.
7. *Bio-luminescence*: This is a special case of chemi-luminescence brought about by oxygen and an enzyme such as luciferase during certain fermentation reactions.

*Cause of Luminescence* :—

Though the exact cause of luminescence is debatable, the phenomenon can be attributed to certain groups of co-ordinated atoms known as "phosphors" present in a crystalline substance. Phosphors are related to luminescence in the same manner as chromophores to colour. Luminescence is associated with the presence of co-ordinated groups of "intruding atoms termed centres." According to De Mint<sup>3</sup>, "the phenomenon is to be ascribed to the active centres furnished by the impurities due to cracks in the crystal lattice or vacant lattice positions. Strains in the crystal due to distortion behave as impurities since these impurities introduce additional localised levels of sharply defined

energy." Thus spectroscopically pure zinc sulphide is neither fluorescent nor phosphorescent, but if it is heated to 800-900°C for about 30-120 minutes in an atmosphere of hydrogen or air, it becomes luminescent. Further in case of zinc sulphide, copper acts as an accelerator. The activation by copper is ascribed to its incorporation in the crystalline structure of the phosphorescing substance. Copper, even when present to the extent of only 0.005%, can bring about activation of zinc sulphide.

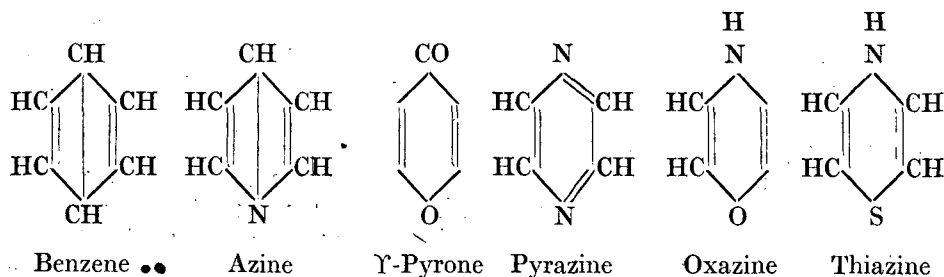
*Theory of fluorescence* :—

There is as yet no theory which satisfactorily accounts for all the facts known about fluorescent substances. A few theories which have been put forward are discussed below :—

1. *The Fluorophoric Theory of Meyer* :—

This theory corresponds to that of Witt for the cause of colour among organic compounds. Meyer ascribes fluorescence in organic compounds to existence of "fluorophors" in much the same way as Witt ascribes colour to "chromophores."

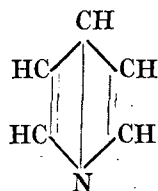
The following structures are described by Meyer as fluorophors :—



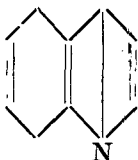
According to Meyer, the presence of a single fluorophor by itself is not adequate to induce luminescence. The

fluorophor should be suitably augmented by fusion with other aromatic fluorophoric nuclei. In support of his theory

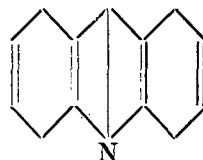
he quotes the example of pyridine which does not give fluorescent derivatives in contrast to quinoline and acridine derivatives which are fluorescent.



Pyridine



Quinoline

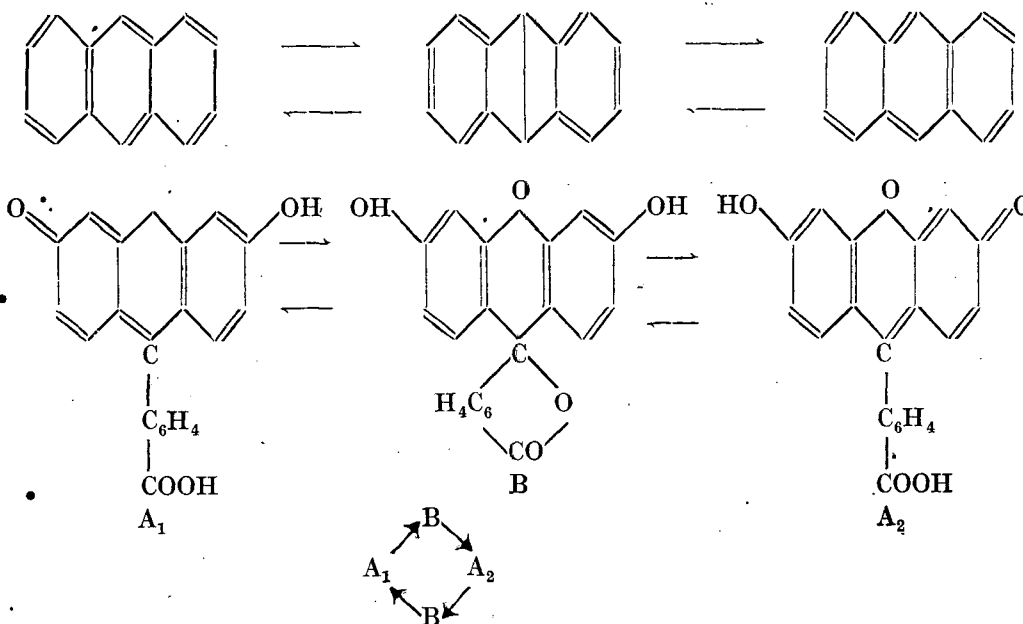


Acridine

### 2. The Tautomeric Theory of Hewitt :—

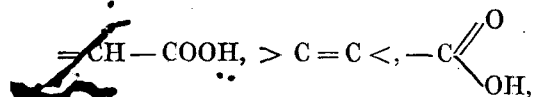
Hewitt postulated that only those substances which could exist as tautomers

were fluorescent. He ascribed the luminescence of anthracene to its ability to assume one of the following configurations :—



### 3. The Luminophoric Theory of Kaufmann :—

Kaufmann attributed fluorescence to certain groups in the molecule which he called "luminophors." The substances in which these groups produce fluorescence were called "fluorogens." Examples of luminophors are :—  $>C=O$ ,  $-C\equiv N$ ,



conjugated ethylenic bonds, benzene ring, *o*- and *p*-quinonoid rings, azomethine group ( $-CH=N-$ ) and conjugated azomethine groups.

Thus Meyer associates  $\gamma$ -pyrone ring with fluorescence and the latter becomes evident when the  $\gamma$ -pyrone ring is fused with benzene rings on either side. Kaufmann, on the other hand, regards benzene ring as the luminophor and the conversion of its potential luminescence into emission as due to its substitution in the  $\gamma$ -pyrone ring.

### Relation between constitution of dyes and fluorescence:—

Dyestuffs which are deeply coloured seldom exhibit fluorescence. On the other hand pale coloured dyestuffs like pink, lilac, blue, orange and yellow dyes fluoresce well if they possess characteristic structures. Quinolines, acridines, xanthenes, phthalins, primuline and thioflavines exhibit strong fluorescence.

Acridine or thiazole dyes containing a sulphonic group fluoresce well. Naphthalene derivatives show better fluorescence than benzenoid compounds. Although the nitro and hydroxyl groups depress fluorescence, azo dyes containing these groups show good fluorescence; for instance, the dyestuff obtained by coupling diazotized *p*-nitroaniline with  $\beta$ -naphthol. Quinone-oximes show little of this property. Some of the monazo, disazo, trisazo and tetrakisazo dyestuffs show good emission. Stilbenes and pyrazolones show fluorescence. Pyronines, xanthenes, diphenylmethane and triphenyl methane dyestuffs are all fluorescent. Quinolines and acridines show fluorescence mostly between yellow and red.

Some dyestuffs fluorescing strongly in the blue region are encountered in the oxazines and thiazines group of dyes. A few dyes derived from anthraquinone are also fluorescent. It is however found that the Indigoids do not luminesce readily. Most of the dyes occurring in nature fluoresce strongly.

### Effect of substitution:—

No general rules can be laid down as regards the relation between luminescence and substitution in organic compounds. The influence of substitution depends on the nature of the substituent and the position it occupies in the molecule. Roughly, however, groups like  $-\text{OH}$ ,  $-\text{OCH}_3$ ,  $=\text{CH}_2$ ,  $-\text{CN}$ ,  $-\text{NH}_2$  increase intensity of illumination and

shift the radiation to higher wavelengths. Groups like  $=\text{CO}$ ,  $-\text{COOH}$  weaken luminescence. Groups like  $=\text{CO}$  and  $-\text{OH}$ , if present in the same molecule, neutralize each other's effect. Halogens introduce centres with deficit energy content and decrease fluorescence without shifting the wavelength. Conjugated double bonds intensify fluorescence. The above generalizations are confined to luminescence in the visible region.

As regards emission in the invisible region, groups like  $-\text{SO}_3\text{H}$ ,  $-\text{OH}$ ,  $-\text{C}=\text{O}$ , etc., intensify luminescence, whereas groups like  $-\text{NO}$ ,  $-\text{NO}_2$  have a tendency to quench it.

The effect of substitution by a metallic cation is to quench the fluorescence.

Attachment of an  $-\text{OH}$  group para to the nitrogen atom of aromatic structures is attended with intensified luminescence.

### A few applications of luminescent dyestuffs:—

Some acid and basic dyestuffs which have a tendency to fluoresce under irradiation by mercury vapour lamps are used for dyeing silk fabrics which are to be displayed at night.

A few compounds derived from stilbene are substantive to textile fibres and in addition absorb invisible radiation and re-emit it as pale-blue in the visible region. These products are used commercially as optical bleaching agents. A few examples are: Tinopal BV (Gy), Uvitex RS (Ciba) and Uvitex WS (Ciba). The latter has affinity for wool and silk and the former for cotton. They are applied to cotton, wool and silk in a manner similar to direct dyestuffs. Since the compounds have affinity and are stable to conditions existing in the dye-bath, they can be added to the dye-bath itself. They are, however, seldom used on dyed goods and their use is mostly

confined to bleached goods. Dyes like fluorescein which exhibit very strong luminescence are used to trace the source of streams and rivers. Hundreds of airmen stranded over the seas owed their rescue to this dyestuff since a small quantity of the same dropped into the water left a streak of a brilliant red colour in the water which could be observed from thousands of feet above. Fluorescent dyestuffs are also used in the army to maintain contact between the ground and the air. In this connection it is observed that fluorescent dyestuffs have an advantage over the ordinary brilliant basic dyestuffs. The method adopted is to spread panels dyed with fluorescent dyes on the ground and spot them from the air. The use of brilliant dyestuffs depends on reflection which would be pronounced at a given angle of incidence and reflection. For maximum visibility the angle of observation has to coincide with the angle of reflection and both will depend on the direction of the sun. An emissive dyestuff, on the contrary, sends out radiation in all directions so that this offers more chances of recognition. Further, the emission is governed by the Beer law which states that the emitted radiation must be of a longer wavelength than the incident radiation. This is a direct corollary to the general law of the conservation of energy which stipulates that the energy output cannot exceed the energy input. Thus the dyestuff which absorbs in the lower ultra-violet region will emit radiation in the visible region. Some of the basic dyestuffs like Rhodamines fulfil the requirements.

Luminescent pigments find use in the identification of friendly armour and equipment in the dark. Zinc sulphide is the pigment most often used for these purposes.

*Fluorescence and fading of dyes and their photochemical activity :—*

Most fluorescent dyestuffs fade badly

and, in addition, fabrics dyed with fluorescent dyestuffs are tendered on exposure to sunlight. The phenomena of fluorescence, fading and tendering appear to be inter-related but the nature of the precise relationship is not clear. A few fluorescent dyestuffs such as Duranol Red G and Duranol Brilliant Yellow 6G which are capable of bringing about perceptible tendering of substrates like acetate silk or nylon, however, do not fade readily (light fastness—4-5). It is suggested that in fading<sup>5</sup>, dissociation of the dyestuff occurs in the presence of light, air and moisture. Nicholls and Merit<sup>3</sup> have detected increased electrical conductivity in fluorescing solution of dyestuffs under illumination. This is difficult to reconcile with the Rule of Structure Integrity proposed by De Mint which states that dissociation and fluorescence do not occur simultaneously<sup>3</sup>.

So far as the basic dyestuffs are concerned, fading has been attributed to the presence of oxonium, sulphonium and ammonium groups present in these dyestuffs<sup>6</sup>.

*Attempts to increase stability of the fluorescent dyestuffs to light :—*

Although the fastness to washing can be improved by after-treatment of the dyeing with cationic softeners<sup>6</sup>, this treatment results in the lowering of the fastness to sunlight. The treatment involves the conversion of trivalent nitrogen into the pentavalent state as in the case of basic dyestuffs, which are fugitive to light. The usual method of enhancing the fastness of the basic dyestuffs by treatment with phosphotungstic acid, tannic acid, etc.,<sup>6</sup> is effective in so far as the dyestuff in the form of the metal-lake is more stable to light, but the fluorescence of the dye is lost due to the introduction of the metallic atom in the molecule<sup>3</sup>.

An after-treatment with melamine-formaldehyde monomer<sup>7</sup> has been found

Very useful since the formation of the resin film on the surface of the dyed fabric may effectively shield the dyestuff by selective absorption of the radiation responsible for degradation. A resin film using guanidine carbonate has also been found very effective. Recently, a plastic based on sym. dimethyl glycol has been found quite useful in ensuring better stability of basic dyestuffs like Methasol Aurine AS<sup>3</sup>. Some of these treatments are quite restrictive and hence no method can be universally recommended.

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## Ion-Exchange

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IN 1856, J. Thomas Way<sup>1</sup>, a consulting chemist to the Royal Agricultural Society of England discovered that the apparent bodily removal of ammonia from aqueous solutions on passing through certain soils was really an exchange with the calcium of a particular type of silicate occurring in these soils. Eichorn discovered that this exchange was reversible. Subsequent researches on the cation-exchange properties of the soils and humus materials led to the commercial application of zeolites and acid-treated coal to water-softening and to the development of synthetic gel zeolites. However, till 1935 the application of ion-exchange was limited to the field of water-softening only. This was not because the phenomenon was not well understood but because of the limitations of the then available ion-exchange materials—the main limitations being their low capacity and chemical instability under extreme pH conditions.

A new era in the field of ion-exchange dawned with the discovery by Adams and Holmes<sup>2</sup> in 1935 that resins of the phenol-formaldehyde class exhibited ion-exchange properties. The advantages of these synthetic resins were not only the higher operating efficiency, better mechanical, chemical and thermal properties but also that they could be made with "tailor-made" properties to suit any particular application by selecting proper reactants for the polymerisation reaction. Since 1935, the advance has been very rapid and the ion-exchange principle has been applied so very extensively in the field of technology that ion-exchange is now considered as a unit operation.

The phenomenon of ion-exchange can be defined as the exchange of ions that occurs on contacting an ionic solid with an electrolyte. The ionic solid is called the ion-exchanger. Ion-exchangers

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