The real point of my story is that industry the world over needs technical men, more than it can get. The reason is that people the world over want more and more of the good things in life, faster than industry can devise them or turn them out. The technical man who is soon to take his place in industry has a wonderful opportunity to make a place for himself.

He also has a wonderful opportunity to serve others. People aren't mere economic entities. There is a need to let them see constantly that industry regards them as human beings, that it wants their confidence, and that our kind of world deserves their faith. Industry will have to receive a great deal of help from you in meeting that responsibility.

What industry can give its employees depends primarily on what the employees, through their efforts, make of industry. This is true because, from the employees alone comes the vitalizing force, the yeast that gives life and energy to such inert ingredients as capital and raw materials, and determines the amount and kind of benefits that can flow to all concerned.

Sodium Chlorite—A New Bleaching Agent.

S. SUNDARAM*

COTTON fabrics and yarns as received in the fininshing department are discoloured and difficult to wet, due to impurities like fats and waxes, pectins, starch and coloured bodies. These impurities seriously interfere in the bleaching and dyeing operations and hence necessitate their thorough removal. A good bleaching must impart to the goods a pure and permanent white and level dyeing properties without tendering or diminishing their textile quality. It is also necessary that the bleached goods should have a good absorbency and a low ash content.

5.

Prior to scouring, desizing is carried out on the goods to remove the starch and other soluble impurities. The process is usually to impregnate the cloth with mineral acid or with hydrolytic enzymes.

Scouring is the process where the pectins, proteins and waxes are removed by the combined action of alkali, soap or

other detergents at a high temperature under pressure. This boiling treatment takes usually six to twelve hours depending upon the quality of the material treated.

Scouring is followed by bleaching. Sodium hypochlorite or bleaching powder is commonly employed as bleaching agent.

Hypochlorites are very powerful oxidising agents and strict control is necessary when bleaching is done with them. They not only oxidise the colouring matter and impurities but also transform cellulose into oxycellulose. Hypochlorites also bring about accelerated oxidation. During the bleaching of coloured goods if active vat dyes are present on cellulose and if light falls on the goods, enhanced tendering of cellulose takes place. Though hypochlorite bleach is cheap, it is attendant with all the above difficulties and hence requires careful control

^{*}Demonstrator, Textile Chemistry Section, Dept. of Chemical Technology.

The use of hydrogen peroxide for bleaching is more recent. It is a universal bleaching agent in that it can be used with wool and silk also. Since peroxides act at a high temperature, scouring and bleaching can be combined together. Hydrogen peroxide is catalytically activated by many metals and by mildew. When a local action is allowed to develop in this manner goods are likely to be tendered.

A new bleaching agent, sodium chlorite, marketed under different trade names like Textone, C2, bleaching salt Bayer, etc., is likely to revolutionise the entire bleaching process. The main reason is its advantages over other bleaching agents.

Chlorites are salts of chlorous acid, - ClO₂. Though many chlorites are known only in the laboratory, sodium chlorite is prepared on a commercial scale.

The discovery of chlorite and chlorine dioxide can be traced as far back as 1815. Most of their properties, however, were investigated only after 1915. In the year 1921 Schmidt introduced chlorine dioxide for the removal of incrustants from cellulose from wood. Taylor and co-workers put sodium chlorite into the commercial use of bleaching kraft pulp. This led to the development of chlorite as a bleaching agent for textiles.

Sodium chlorite exists in anhydrous and trihydrate forms. It is slightly hygroscopic but does not cake on stor-

age. In the pure state its available chlorine is about 157 per cent compared to about 35 per cent in bleaching powder. Another added advantage is its stability as a solid as well as in aqueous solutions.

When heated, chlorite decomposes mainly into chlorate and chloride. A small proportion also decomposes as chloride and oxygen.

 $\begin{array}{rcl} 3 & \operatorname{NaClO}_2 \rightarrow & 2 & \operatorname{NaClO}_3 + \operatorname{NaCl}.\\ & \operatorname{NaClO}_2 \rightarrow & \operatorname{NaCl} + \operatorname{O}_2 \end{array}$

Solutions of sodium chlorite are very stable provided they are not acidic. In fact they show no oxidising ability above pH7. On acidification, chlorous acid is produced, the ionisation constant of which is 1.1×10^{-2} . The free chlorous acid decomposes into chlorine dioxide, chloric acid and hydrochloric acid. This happens near about pH 2 e.g. $4HClO_2 \rightarrow 2 ClO_2 + HClO_3$ + HCl + H₂O.

Hypochlorite under alkaline conditions is a stronger oxidising agent than chlorite under acid conditions. The activity of chlorite.

(i) increases with a decrease in pH. (ii) increases with temperature and (iii) increases with concentration.

Strong acids must not be allowed to come in contact with chlorite since the large quantity of ClO₂ evolved is liable to explode under sufficient concentration. Chlorite reacts vigorously with sulphur. Hence use of sulphur-bearing articles like rubber is to be avoided. Neoprene can be used safely with chlorite.

Chlorite under acidic condition is a specific oxidising agent for aldehydic groups. Its reaction with various carbohydrates have been examined and chlorous acid seems to be the oxidising agent.

R-CHO+3 HClO₂ → R-COOH +2 ClO₂+HCl+H₂O.

Chlorite can be rendered active by acids, hypochlorite, and chlorine.

When acidified to about a pH 3-5 chlorite decomposes as

 $5 \text{ NaClO}_2 + 4\text{HCl} \longrightarrow$

$$4\text{ClO}_2 + 5\text{NaCl} + 2\text{H}_2\text{O}$$

This reaction is used in the bleaching of textiles. Within pH limits of 8-9 chlorite reacts with hypochlorite giving ClO_2 .

 $\begin{array}{l} 3\text{NaClO}_2 + 2\text{HClO} \rightarrow 2\text{ClO}_2 + \text{NaClO}_3 \\ + 2\text{NaCl} + \text{H}_2\text{O}. \end{array}$

Within pH limits of 9-10 there is tendency for ClO_2 to react further with hypochlorite.

 $2NaClO_2 + HClO \rightarrow 2ClO_2 + NaCl + NaOH$

$$2\text{ClO}_2 + \text{NaOH} + \text{HClO} \rightarrow 2\text{HClO}_3 + \text{NaCl}.$$

This reaction makes bleaching less efficient. When the pH is still higher, chlorite is converted into chlorate with practically no chlorine dioxide formation.

$$NaClO_2 + NaClO \rightarrow NaClO_3 + NaCl$$

A chlorite-hypochlorite mixture can be used to bleach textiles at a pH between 8 and 9 at room temperature with the usual equipment for hypochlorite bleach. From actual trials it has been found that chlorite-hypochlorite mixture in the ratio of 1:1.5 (in terms of available chlorine) is the most suitable for bleaching purposes.

When chlorine gas is passed into chlorite solutions, ClO_2 is formed according to the equation :

 $2NaClO_2 + Cl_2 \rightarrow 2 ClO_2 + 2NaCl^{\bullet}$

This reaction is commercially used in the bleaching of wood pulp for paper manufacture and in the production of chlorine dioxide.

The addition of aldehydes and acetone activates chlorite at a neutral pH. Persulphates, peroxides, finely divided metalloids and hydrolysable chlorinated organic solvents also activate chlorite, liberating chlorine dioxide.

Since chlorite is an active bleaching agent in acid medium, it is an ideal bleaching agent for acetate rayon. Chlorite has also been used in stripping dyed nylon and in oxidising vat and sulphur colours.

Sodium chlorite also finds use in many other industries as a bleaching agent as shown below :

- (i) Bleaching paper pulp.
- (ii) Bleaching other cellulosic materials like straw, oat hulls, hemp, etc.
- (iii) Bleaching grease, tallow, sugar, oleic acid, starch, nylon, alginic acid, yellow laundry soap, bees wax, coco butter, soya bean oil, etc.

There are many advantages with chlorite as a bleaching agent. Chlorite has minimum attack on cellulose during bleaching. During bleaching of coloured fabrics chlorite brings about no accelarated oxidation of the type which occurs with hypochlorite. The oxidiation potential of chlorite is much lower than that of hypochlorite, but sufficiently high to oxidise natural impurities and coloured bodies in cellulose and too low to oxidise cellulose itself. Chlorite liberates chlorine dioxide rather than free chlorine, the destructive action of which on allulose is well known. Even boiling solutions of chlorite having twice the con centration as used commercially have destructive action on cellulose. •Stringent 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.

REFERENCES :

- 1. White ct. al., Ind. Eng. Chem., 1942, 34, 782.
- 2. Taylor et al., Ibid., 1940, 32, 899.
- Dubeau and others, Amer. Dyestuff Rep., 1939, 28, 590.
- 4. Vincent et al., Ibid., 1941, 30, 358.
- 5. B.P. 519, 561.
- 6. B.P. 380, 488.
- 7. Skinners Silk and Rayon Record, 1952, 26, 977

Luminescence, Luminescent Dyes and Pigments

S. P. CHANDAVARKAR*

THE glowing of phosphorus in the dark is known as "phosphorecence." 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 stabil-

ity 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.1 Unlike in phosphorescence, in fluorescence the activated electron is unstable. Both these phenomena are " luninescence."2 covered by the term The two phenomena have, however, little in common. Thus photo-conduct-ivity-the increase in electrical conactivity 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.

^{*}Assistant Registrar, Department of Chemical Technology.