

This concept explains why *pitting* is more marked in steels of nonuniform surface structure (areas of differing potential) than when the surface is uniform, *although the actual corrosion, which is determined by oxygen diffusion over the total area, is the same.* Similarly, the corrosion of steel in salt solutions results in pitting, since the increased conductivity creates a larger area of hydrogen deposition and depolarization from a central point of attack.

In the case of imperfect coatings of lower metal on steel, such as exist in copper, lead, or tin plate, the amount of corrosion at the point of imperfection is determined by the amount of depolarization afforded by the adjacent plated area. It should, therefore, be possible to calculate the depth of pitting which results from the concentration of this corrosion on a very small area of steel.

## Sulfuryl Chloride<sup>1</sup>

### I—Principles of Manufacture from Liquid Sulfur Dioxide

By Ralph H. McKee and Carroll M. Salls<sup>2</sup>

COLUMBIA UNIVERSITY, NEW YORK, N. Y.

NEW uses for any article of commerce are naturally of interest to manufacturers of that article. When the article happens to be a by-product or a waste product, the question of uses assumes greater importance. In some cases where uses have been found for a by-product, the whole process has been stimulated to greater production because part of the profits realized on the by-product have been applied for the purpose of underbidding competitors on the principal product. Competition eventually eliminates profit, but as that state of equilibrium is approached the cost of the principal product is decreased to such a degree that entirely new fields of technology may be opened up in which the principal product can be applied.

Sulfur dioxide and chlorine are both by-products of large-scale operations and, in addition, their toxic action makes it difficult to throw either material away even when that is economically possible. Consequently, a simple method of combining these two materials to make a useful product should be of interest to producers of both materials.

Brallier<sup>3</sup> has recently expressed the urgent need of finding new tonnage uses for chlorine. Over one-half of the installed capacity of the country is lying idle and there is no prospect of utilizing more than a small fraction of this idle equipment. After a review of the production statistics for chlorine products and analysis of possible outlets for chlorine, this author expresses the opinion that manufacturers of chlorine should make a cooperative effort to develop products that will provide some return on the millions of dollars of capital now invested in chlorine plants. Such constructive and united action has certain undeniable advantages in the direction of education of consumers, and it might lead to the building up of consuming capacity to the present producing capacity, or even further.

As for sulfur dioxide, the Chandler Lecturer for 1923<sup>4</sup> at Columbia University brought out very forcibly the reasons for the endless litigation directed against smelter operators by the pooled agrarian interests of the community. One

*Sulfuryl chloride has been one of the medium priced chemicals, but one which, if the cost were cheap enough, would have a much more extensive use.*

*Basing their work on the modern theories of contact catalysis, the authors have worked out a new method for the manufacture of sulfuryl chloride which promises to place this chemical industrially in the "heavy chemical market" class. Over 99 per cent yield of 98 per cent purity sulfuryl chloride is obtained by direct combination at room temperature in iron apparatus of pure sulfur dioxide and chlorine, and removal of the catalyst by filtration.*

large smelter discharged daily through a single tall stack several thousand tons of sulfur dioxide gas among other waste products. Sulfur dioxide from smelting operations of this kind has injured vegetation for miles around and polluted the air of nearby towns. Consequently, it has been profitable to wash a part of the

stack gases and sell the sulfur dioxide in the form of liquid for the cost of recovery. One smelter (Tacoma, Wash.) has sold liquid sulfur dioxide to paper manufacturers at \$12.00 a ton.

It is true that combination with chlorine could at best utilize only a small part of this sulfur dioxide, but it might at least mitigate the nuisance of one of the smaller smelters to such a degree as to satisfy the demands of the community.

The writers' investigation has developed a method for the manufacture of sulfuryl chloride which they believe to be much cheaper than methods hitherto used, possibly cheap enough to permit the manufacture of sulfuric acid and hydrochloric acid from it by the addition of water.

When produced at this cost, a long list of applications of this remarkably active chemical would be opened up. Sulfuryl chloride is a vigorous chlorination agent, producing in general—not always—the same products as elementary chlorine. It will be shown in a subsequent article that it is especially applicable in gaseous reactions such as the chlorination of methane, because the reacting mixture cannot explode and undesirable reactions are much more easily controlled. The use of sulfuryl chloride in the manufacture of acetic anhydride has the advantages of forming less chloroacetic acid, of supplying exactly the molecular proportions required by the reaction, of eliminating the necessity of removing free sulfur from the product, and of a price differential due to the fact that one of the present processes uses liquid sulfur dioxide and liquid chlorine whereas sulfuryl chloride can be produced, if desired, by the combination of sulfur burner gas with the chlorine as it leaves the electrolytic alkali cells. Chlorosulfonic acid—a material for which there is some demand—can be readily made directly from sulfuryl chloride. Like sulfur chloride,  $S_2Cl_2$ , sulfuryl chloride,  $SO_2Cl_2$ , vulcanizes rubber; but as yet no method of controlling the action to avoid the production of a brittle product has been found. The literature describes many other po-

<sup>1</sup> Received August 25, 1923.

<sup>2</sup> Goldschmidt Fellow. Paper submitted in partial fulfillment of the requirements for the degree of doctor of philosophy, Department of Chemical Engineering, Columbia University.

<sup>3</sup> *Chem. Met. Eng.*, **28**, 846 (1923).

<sup>4</sup> Swain, *THIS JOURNAL*, **15**, 206 (1923).

tentially valuable reactions of sulfuryl chloride, but the few applications mentioned here show sufficiently well that a cheap method for the manufacture of sulfuryl chloride will be instrumental in finding a use for some of the idle chlorine equipment of the country.

#### OLD PROCESSES

Sulfuryl chloride has been prepared by bringing sulfur dioxide and chlorine together in the presence of ethylene,<sup>5</sup> camphor,<sup>6</sup> acetic anhydride,<sup>7</sup> and many other organic compounds such as esters, terpenes,<sup>8</sup> formic acid, glacial acetic acid, charcoal,<sup>9</sup> etc. It is formed slowly when a mixture of chlorine and sulfur dioxide is exposed to sunlight, and more easily by heating chlorosulfonic acid in the presence of a catalyst.<sup>10</sup> It is commonly prepared technically by adding liquid chlorine gradually to liquid sulfur dioxide in which camphor has been dissolved.<sup>11</sup> Pope<sup>12</sup> makes the charcoal method continuous by passing equimolecular proportions of chlorine and sulfur dioxide into a reaction chamber packed with chunks of charcoal, but the method is not one that lends itself to production on a manufacturing scale. The sulfuryl chloride is drained off the bottom or removed as a vapor. Pope says, "due to the low thermal conductivity, it is difficult to maintain a uniform temperature throughout the catalyst in the mass of which the reaction is taking place." This matter is important because the yield of sulfuryl chloride decreases rapidly with rise of temperature. Moreover, in the operation of the Pope patent it is necessary to use equimolecular proportions of the reacting gases.

#### NEW PROCESS

Sulfur dioxide and chlorine are continuously dissolved in a body of liquid sulfuryl chloride which carries activated carbon in suspension. When the reacting substances are nearly pure, the combination takes place rapidly and completely at room temperature. The carbon catalyst effects the combination of the dissolved substances, thus producing fresh solvent. Sulfuryl chloride is removed from the carbon by filtration, and the liquid is run directly into iron drums for shipment. Measurement of gases is avoided by the use of a volume of sulfuryl chloride sufficiently large to dissolve the total supply of either gas for several hours if necessary. When dilute gases are used, it is preferable to reduce the vapor pressure of the sulfuryl chloride in the catalyzing chamber by cooling to 0° C. or by adding a solvent. Sulfuryl chloride vapors are removed from the exit gases by absorption in a solvent such as chlorosulfonic acid or pentachlorethane.

Since the carbon effects the reaction by virtue of selective surface action, it is obvious that the process is subject to the ills that attend contact catalysis. It is therefore important to point out as clearly as possible the action of the catalyst under the conditions of this process. The writers have succeeded in defining the peculiar conditions that govern the selection and use of a catalyst having a high activity and a long life.

#### CATALYSIS BY ACTIVE CARBON

Within the past few years several types of highly activated carbon have been put on the market at a reasonable

<sup>5</sup> Regnault, *Ann. chim. phys.*, **69**, 170 (1838).

<sup>6</sup> Schultze, *J. prakt. Chem.*, **24**, 168 (1881).

<sup>7</sup> Aktien-Gesellschaft f. Anilin Fabrik, German Patent 226,218 (1909).

<sup>8</sup> Durrans, British Patent 124,542 (1918).

<sup>9</sup> Melsens, *Compt. rend.*, **76**, 9204 (1878).

<sup>10</sup> Wohl and Ruff, *Ber.*, **34**, 3509 (1901); German Patent 129,862 (1902).

<sup>11</sup> Badische, German Patent 138,531 (1901).

<sup>12</sup> Pope, British Patent 122,516 (1918).

price. It has been known since 1873 that charcoal will catalyze the reaction between sulfur dioxide and chlorine, but in view of Trautz<sup>13</sup> statements that coconut charcoal has almost no action and that two hundred and seventy out of three hundred experiments with animal charcoal had to be rejected, it was not at all certain that these highly activated carbons would be suitable for a commercial process. Behrend<sup>14</sup> reported a very poor yield when charcoal is used as the catalyst, and decidedly preferred the chlorosulfonic acid method. Apparently, there is some fundamental difference in the several types of carbon other than extension of surface which affects their catalytic activity. It seems to be the opinion of those who have had experience with this reaction that the camphor or the chlorosulfonic acid methods are the best. The first method, however, requires two distillations to produce a pure product, and there is a large loss of camphor due to reaction with sulfuryl chloride and sulfuric acid at the temperature required for distillation. The second method does not use elementary chlorine. A thorough study of the fundamental characteristics of the reaction in the presence of carbon has led the writers to disagree with this prior opinion.

Chlorine and sulfur dioxide are quite soluble in liquid sulfuryl chloride.<sup>15</sup> If carbon is added to a saturated solution of chlorine in sulfuryl chloride, the saturation disappears and the temperature of the liquid increases slightly. The liquid is now capable of dissolving more gas. The dissolved chlorine has been adsorbed by the carbon in a manner similar to the adsorption of acetic acid from aqueous solution. The same thing happens in a saturated solution of sulfur dioxide in sulfuryl chloride. If the carbon contains other gases, such as oxygen, nitrogen, carbon dioxide, or hydrogen chloride, they are almost completely displaced when brought in contact with either chlorine or sulfur dioxide. Hence this is an example of selective adsorption. The greater part of the foreign gas is displaced immediately, but the last part is displaced more slowly. The concentration of foreign gas above the carbon must be decreased to a very small value before the last trace is removed.

If sulfuryl chloride is saturated with chlorine and sulfur dioxide in equimolecular proportions and carbon is added, the saturation disappears as before; but in this case it is not possible to saturate the liquid again by slowly passing in chlorine and sulfur dioxide in equimolecular proportions. The solute reacts to produce the solvent. This process goes on indefinitely and the number of grams of carbon per cubic centimeter of solvent continuously decreases, but the velocity of reaction remains constant provided that the concentration of dissolved gases stays constant and that the carbon surfaces remain intact. Consequently, the carbon has appeared in the role of a catalyst.

It may be possible to learn a little more about contact catalysis from this rather novel system. Such information would be of first importance to the writers, not in order to aid in the development of a general theory of catalysis by comparing their results with those of others, but to find out which theory of catalysis best explains the characteristics of this particular reaction. Then the facts that have been gathered around this theory will be more likely to aid in establishing the conditions necessary for the most economical operation of the process.

Faraday's conclusion<sup>16</sup> concerning the combination of gases in the presence of platinum, stated in modern language, is: Two reacting gases are absorbed by the platinum and, being thus brought into intimate contact with each other,

<sup>13</sup> *Z. Elektrochem.*, **14**, 534 (1908).

<sup>14</sup> *J. prakt. Chem.*, [2] **15**, 23 (1877).

<sup>15</sup> Schultze, *Ibid.*, [2] **24**, 176 (1881).

<sup>16</sup> Experimental Researches, Sixth Series, Vol. I, p. 165; also paragraph 361.

proceed to react. Thomson<sup>17</sup> has shown that the surface tension of the absorbed film changes as the chemical reaction proceeds. The physical state of the catalyst itself changes during the reaction. Crystalline manganese dioxide used as a catalyst for the potassium chlorate decomposition becomes amorphous.<sup>18</sup> Clean platinum gauze used as a catalyst in the oxidation of ammonia becomes covered with a spongy deposit. Finely divided metals for hydrogenation change<sup>19</sup> their surface structure. These examples show that there is an interchange of energy between the catalyst and the reacting substances. Consequently, in the case of carbon it is probable that the energy which appears at the surface due to fine subdivision leaves the surface, is added to the driving force of the reaction, and returns to the catalyst when its work is done. This energy would appear as the excess of heat of absorption over heat of compression when there is no substance present with which the absorbed film can react. When a reaction takes place the energy would be returned to the catalyst by release of the product from the high pressure existing in the absorbed film.

Without committal concerning the mechanism of catalysis, we may, for the present, consider a positive catalyst as a substance that is capable of delivering a certain amount of energy per unit of time, and apply it in the same place and in the same direction as the energy that tends to drive the chemical reaction, thus causing an increase in the velocity of the chemical reaction. The mechanism may consist in the formation of intermediate chemical or other compounds, but that is not essential to such a conception of catalytic activity.

A chemical reaction results in a change of spatial relations through the application of forces associated with the constituent particles, the work balance usually appearing as the heat of reaction. The introduction of a time factor gives power. Hence catalytic activity has the dimensions of power.

In general, a small quantity of catalyst is sufficient to act upon a very large quantity of the reacting substances, but the rate at which the reacting substances will be converted does depend on the quantity of catalyst present. A definite quantity of catalyst can supply a certain maximum impulse and no more. The increase in the rate of hydrolysis of methyl acetate by increasing quantities of acetic acid is the best known example of this fact. A change in the extent and character of contact surfaces is known to affect the efficiency of the catalyst in heterogeneous systems.

The impulse supplied to a mixture of chlorine and sulfur dioxide by a unit weight of carbon is much smaller than is ordinarily the case with metallic catalysts—i. e., a comparatively large weight of carbon must be used to produce the same number of pounds of product per hour. One gram of the best carbon working at full capacity will produce 0.5 pound of sulfuryl chloride per hour, whereas 1 gram of platinum will produce several hundred pounds of sulfur trioxide per hour. The necessity for using this comparatively large quantity of catalyst makes it possible to subject the catalyst to ordinary quantitative manipulations such as purification and weighing with a percentage accuracy of the same magnitude as the rest of the experiment, and still keep within the limits of laboratory apparatus in measurements on the product and on the gases which go to make the product. The measurement of the maximum impulse imparted by several types of adsorbent carbon is described below. The fact that the reaction proceeds at a very slow rate in the absence of carbon makes it possible to stop the reaction at any time by a simple filtration through paper. The data

on relative carbon activity supply a standard upon which to base calculations concerning the probable cost for catalyst, capacity per unit volume of reaction chamber space, and the yield of sulfuryl chloride.

#### RELATIVE CARBON ACTIVITY

A saturated solution of chlorine and sulfur dioxide in sulfuryl chloride at 25° C. contains 5 per cent of dissolved gases. At equilibrium at 25° C. sulfuryl chloride contains 1 per cent of dissolved sulfur dioxide and chlorine. Unsaturated sulfuryl chloride dissolves chlorine and sulfur dioxide at a rate far above the capacity of the meters used by the writers.<sup>20</sup> Carbon adsorbs chlorine and sulfur dioxide from a saturated solution very rapidly, but by working with a small sample of carbon it is possible to supply the gases at such a rate that the vapor pressure of the liquid remains at 760 mm.—i. e., the liquid remains saturated. Then the meter readings give directly the rate at which a known weight of carbon is producing a combination of chlorine and sulfur dioxide at any instant.

Although the chlorine and sulfur dioxide gases taken from cylinders were further dried by sulfuric acid and by passing through a tube containing phosphorus pentoxide on glass beads, it was found that the catalytic activity of the carbon gradually decreases, probably due to amounts of impurities too small for detection by the ordinary methods of gas analysis. It may be due to a change in the physical constitution of the catalyst itself, but this is improbable as the carbon can be reactivated by a simple washing and drying.

In order to determine the relative activity of several types of activated carbon, a series of experiments with each carbon was carried out in which the rate of supply of the gases was constant and the weight of carbon changed until the smallest weight was found that would cause the vapor pressure of the solution to remain below 760 mm. for 1 hour. Comparison of the minimum weights of carbon required thus expresses the relative activity of these carbons with sufficient accuracy, considering the large differences that were found.

The chlorine and sulfur dioxide gases from the meters were mixed in equimolecular proportions and passed into a 500-cc. flask immersed in a thermostat at 20° C. The flask contained the same quantity of redistilled sulfuryl chloride in each experiment. The sample of dry carbon was suspended in the sulfuryl chloride. The gas mixture was admitted to the flask through a 3-mm. ( $\frac{1}{8}$  inch) i. d. glass tube at a constant rate of 147 liters per hour equivalent to 453 grams (1 pound) of sulfuryl chloride per hour. This made the linear velocity through the inlet tube 51.5 meters per second. The gases were completely absorbed—i. e., the yield of sulfuryl chloride was approximately 100 per cent of theory. In fact, a slight suction persisted in the outlet tube during the greater part of the experiment. In the absence of a catalyst the amount of liquid taken for each experiment would be, at this rate, saturated with the gas mixture in 2 minutes. Then the gas mixture would come through the liquid unchanged. The gases rising part way through the liquid produced a vigorous agitation. Since the number of grams sulfuryl chloride formed per minute was constant, thermometers inside and outside of the flask showed nearly a constant temperature difference of 10° C.

The minimum weight of catalyst required to bring 453 grams (1 pound) per hour of an equimolecular mixture of chlorine and sulfur dioxide to equilibrium is given in Table I.

Silica gel does not catalyze the reaction between dry chlorine and sulfur dioxide. It adsorbs a gas by virtue of

<sup>17</sup> "Application of Dynamics to Physics and Chemistry," 1888, pp. 206 and 236.

<sup>18</sup> Sodeau, *J. Chem. Soc. (London)*, **77**, 137, 717 (1900); **79**, 247, 939 (1901); **81**, 1066 (1902).

<sup>19</sup> Sabatier, "La catalyse en chimie organique," 1913, p. 55.

<sup>20</sup> Benton, *THIS JOURNAL*, **11**, 623 (1919); Arndt, "Handbuch der physikalisch, chemischen Technik," 1915, p. 230; Oberfell and Mase, *THIS JOURNAL*, **11**, 294 (1919).

capillary attraction only, and therefore the adsorbed film does not make effective contact with the surface. The energy cannot leave the surface.

TABLE I

	Grams
Norit.....	1.8
Darco.....	2
McKee carbon.....	8
Filtchar.....	15
Blood charcoal.....	25
Camphor.....	30
Animal charcoal.....	70
Coconut charcoal.....	75
Whetlerite.....	90
Batchite.....	110
Oak charcoal.....	140
Birch charcoal.....	160
Nitrobenzene.....	600
Silica gel.....	Over 20,000

Inspection of the table shows that those carbons that are capable of delivering a relatively large impulse are all decolorizing carbons, and that acid-treated carbons are more active than alkaline carbons. When the energy exists on the surface of the carbon in the form of a positive charge, there is apparently a greater acceleration of the reaction between negative radicals.

The highly activated carbons that were developed during the war for the purpose of absorbing gases were found to possess comparatively small catalytic activity for this reaction. Decolorizing carbons such as Norit and Darco have about forty times as great activity as a good coconut charcoal obtained from the Edgewood Arsenal. This coconut charcoal had a 40-minute chloropicrin activity, accelerated test. Whetlerite, a copper-impregnated charcoal, had a 30-minute activity, accelerated test.

The great difference between the catalytic activity of gas carbons and decolorizing carbons can be explained on the basis of diameter and length of capillaries. The uncombined chlorine and sulfur dioxide must diffuse through the sulfuryl chloride that fills the capillaries in order to reach the catalyzing surface, where combination takes place rapidly and a corresponding amount of sulfuryl chloride is pushed out of the capillary. When the capillary is long and narrow, as in gas carbons, the solute diffuses to the walls before it can penetrate very far. Hence the bottom of the capillary must be filled with pure sulfuryl chloride and the concentration of solute continuously increases as the entrance is approached. The result is that only the carbon near the entrance of the capillary is exerting its catalytic action. A fish-scale structure, on the other hand, as claimed for Darco carbon, offers much less opportunity for long capillaries, and consequently a much larger proportion of the carbon is active.

The carbon is very easily separated from the sulfuryl chloride by filtration through paper. The sulfuryl chloride runs through faster than clear water. The filtrate is a light yellow, transparent liquid containing over 98 per cent  $\text{SO}_2\text{Cl}_2$ . The remainder is free chlorine and sulfur dioxide. This is pure enough for most purposes, but if a still purer product is desired the liquid may be distilled and the first 20 per cent of the distillate reworked. The remaining 80 per cent distills between  $60^\circ$  and  $70^\circ$  C. as a water-white distillate. There is no distillate above  $70^\circ$  C. The pure product may be distilled with less than 1 per cent loss, showing that sulfuryl chloride is a stable compound. No evidence of decomposition could be detected in several 8-pound bottles that had been standing for 2 years in diffused sunlight.

#### CATALYST POISONS

Moisture, sulfuric acid, chlorosulfonic acid, and nitrobenzene poison the catalyst. Carbon tetrachloride, pentachlorethane, tetrachlorethane, benzene, kerosene, etc., do not poison the catalyst. Moisture hydrolyzes some of the

sulfuryl chloride, producing sulfuric acid, which forms a protective film over the surface of the carbon. A catalyst that has been poisoned by the addition of water can be completely regenerated by washing thoroughly with water and then drying in any suitable manner. Suitable methods of drying are: heating at  $150^\circ$  C. preferably *in vacuo*; heating to  $500^\circ$  C.; heating in a current of a dry gas such as hydrogen chloride, air, chlorine, sulfur dioxide, or carbon dioxide; washing with alcohol and ether. Absorption of moisture from the air can be prevented by saturation of the dried catalyst with chlorine. This also prevents scattering of the catalyst when sulfuryl chloride is added. Since a good grade of decolorizing carbon can be obtained for 7 cents a pound, it is probably advisable to throw the catalyst away when it becomes inactive. Table I shows the cost for catalyst should be less than 40 cents per ton of sulfuryl chloride.

#### MATERIALS OF CONSTRUCTION

Sulfuryl chloride has almost no action on iron at room temperature. The same applies as well to dry sulfur dioxide and dry chlorine. In the experimental work iron vessels in continuous service for months have shown almost no corrosion. Sulfuryl chloride is commonly shipped in ordinary sheet steel drums.

#### COST OF OPERATION

Simplicity, small capital investment, and flexibility of operation are the outstanding features of the equipment required for the manufacture of sulfuryl chloride from liquid sulfur dioxide. The total cost of operation, which includes the cost of the carbon at 7 cents a pound, water, steam, and air, labor at \$5.00 a day, repairs, overhead, interest on investment at 6 per cent, and amortization over a period of 3 years, is estimated at about \$10.00 per ton of sulfuryl chloride on a production of 10 tons of sulfuryl chloride per day. Taking 5 cents per pound as the cost of liquid sulfur dioxide in ton lots and 2.5 cents for chlorine as it comes from the cells, the cost of sulfuryl chloride by this new process should be less than 5 cents per pound.

If sulfuryl chloride is to be used to make hydrochloric acid, liquid sulfur dioxide is too expensive at the present time. In another paper the use of the cheap sulfur burner gas in the manufacture of sulfuryl chloride will be described.

#### Wood Blocks to Measure Soil Moisture

The study of soil moistures has heretofore largely been left to laboratory investigators and omitted from forest field work because of the absence of any successful methods of measuring the moisture applicable to the field. Recent experiments, however, have introduced a method of field measurements which appears to be both simple and effective. W. G. Wahlenberg, forest examiner at the Priest River Forest Experiment Station in Montana, has for some time been employing cypress blocks for this purpose. These may be left in the soil for a short time and may then be easily remeasured. The blocks are very carefully air-dried before being used, and therefore absorb water very readily. The resultant changes in volume are read with the help of a micrometer. A definite relation exists between the swelling of the blocks and the amount of water absorbed, and it is believed that a corresponding relation can be worked out with the soil moisture content. Mr. Wahlenberg has obtained similar results with an ordinary lead pencil, left in the soil for a time and afterwards weighed.

#### Course in Dye Testing

Persons desiring to take the laboratory course in textile chemistry and dyeing which is being given two evenings per week at the Brooklyn Technical Evening School, should register at once. The course will comprise the methods of dye testing, application of all classes of dyes to all fibers, fastness test, color matching, properties of textiles, etc. The instructor is one of the dye experts of the U. S. Government, passing on the competitiveness of imported dyestuffs.