PAPERS READ BEFORE THE BRANCHES OF THE AMERICAN PHARMACEUTICAL ASSOCIATION

DYESTUFF STATISTICS.*

BY BENEDICT SALKOVER.

The following is a résumé of present-day articles upon that most interesting and all-absorbing topic, "Dyestuffs." The fundamental purpose of this paper is not to present anything original, but to bring home a few facts to you concerning products which play a tremendous rôle in the commercial and scientific American world of to-day. Most of the information has been gleaned from the reports of Dr. T. H. Norton, Commercial Agent of the Department of Commerce.

When coal undergoes destructive distillation in coke ovens or gas retorts, the average products are as follows: Coke 72 percent, gas 22 percent, tar 6 percent. The tar contains some 155 different chemical compounds, none of which are dyes. Ten of these substances are utilized in the manufacture of dyestuffs. They are benzol, toluol, xylol, phenol, cresol, naphthalene, anthracene, methyl anthracene, phenanthrene and carbazol, the latter being a constituent of anthracene. The crude gas given off on distillation contains the first three to some considerable extent. Special purifiers have been designed for their removal and separation. The ten substances enumerated form, from 6 percent to 12 percent of the coal tar, the amounts present varying with the character of the distillation.

These ten crude coal-tar products are separated from one another, and from the great variety of carbon compounds accompanying them in the tar, by fractional distillation, which method, as you know, makes use of the different boiling points of various substances for their ultimate separation. From the ten so-called "crudes" chemical works of a high character prepare nearly 300 so-called "intermediates," compounds that are not dyes, but which are susceptible by direct reaction with proper reagents of being transformed into coloring matters. A number of these "intermediates" are used also in the manufacture of medicinal preparations and photographic chemicals. Leading intermediates are: aniline oil and salts, pure aniline and toluidine, nitrobenzol, naphthol, phthalic acid, salicylic acid, resorcinol, anthraquinone, etc. These intermediates are in reality the raw material for the dyestuff manufacture. Out of them over 900 different dyestuffs are made and currently sold throughout the world. It has been stated in a general way that the average intermediate sells for five times as much as the average crude, and the average finished dye for ten times as much as the average intermediate; so you see the average finished dye is worth fifty times as much as the average crude, a very material enhancement in value. Less than three hundred intermediates have been found sufficient to meet the needs of dyestuff manufacturers, these necessarily combining technical with economic advantages. Likewise, of the more than a million dyestuffs covered by patent specifications, only 900 have won a recognized position, and of these only 400 are in great and varied use.

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It has been stated that it is very doubtful whether many additions of value will be made to the current list of dyestuffs in the immediate future. The field certainly has been thoroughly worked, as is easily demonstrated by the number of patents existing at present. During the last ten years only one new class of dyes has been discovered and placed on the market. Dr. Norton, in summarizing the coal-tar dyestuff industry, gives the following features as essential to success: 1. The presence of an ample supply of coal. 2. The extensive use of this coal for gas and coke manufacture. 3. The use of a plant that allows the recovery of the volatile organic compounds formed during destructive distillation. 4. The industrial treatment of the tar produced, so as to separate and furnish in a fairly pure form the ten crude substances. 5. The existence of a well-equipped chemical works, able to transform the ten crudes into nearly 300 more complex intermediate compounds. 6. The existence of a highly organized works for manufacturing from these intermediates some 900 different dyestuffs. 7. An ample and sure supply of a variety of acids and heavy chemicals for affecting the numerous transformations. 8. A relatively large number of university trained chemists.

It may be interesting at this point to consider the manufacture of one intermediate and one dye, just to show the complexity of the reactions involved and the magnitude of the task. Magenta is one of the most famous of red dyes. In its manufacture three intermediates are employed, *viz.*, aniline, toluidine, and nitrobenzene. The toluidine used is of the commercial variety, consisting of 64 percent of the ortho modification and 36 percent of the para. In order to manufacture it, toluol is the first constituent necessary. It is made by distilling one of the coal-tar fractions, boiling between 82° C. and 110° C., containing benzol and toluol. The fact that it has a higher boiling point than benzol is employed in the fractionation. The next step in the process is the manufacture of *o*- and *p*-nitrotoluol, which is done by the nitration of toluol; *o*- and *p*-toluidine are then made by reduction of nitro-toluol with tin and concentrated hydrochloric acid. Calculated amounts of aniline and toluidine are mixed together in a porcelain container in the manufacture of magenta, and a definite amount of HCl is added. The mixture of the hydrochlorides is heated to 130° C., when it is transferred to another container in which is present definite amounts of aniline, toluidine, and nitrobenzene. The mixture is heated, usually on an oil bath, to about 100° C., when a theoretical amount of $FeCl_3$ is added. The container is now connected with an air condenser, and the temperature is gradually raised to 180° C., which is maintained for eight hours. After this the mixture is distilled with steam, when the distillate of red oil and nitrobenzene passes over. The melt is now poured into boiling water of known amount, well stirred, and HCl is added. When acidity is obtained, sodium chloride is added and the whole boiled for a short interval. The aqueous solution, which is poured off, contains the hydrochlorides of aniline and toluidine, which, as well as the previous distillates, is commercially used again in the manufacture. The green residue, brittle after cooling, is extracted with boiling water, acidulated with HCl, which dissolves the magenta. Salt is then added to the filtered magenta solution; after standing some time the crude magenta is salted out by this means, and is recrystallized from water containing HCl. The filtrates from the purification of magenta are worked up commercially and sold under the names maroon, cerise, etc. Magenta, chemically known as "homorosaniline

chloride," dyes silk and wool bluish red directly, and cotton, after having been mordanted with tannin and tartar emetic.

In European coke works, especially in Germany, where nearly all the by-products are saved and utilized, modern recovery ovens with condensation plants have a much more universal use than in this country. The majority of the coke plants in the United States have been in the past and, although conditions have been recently materially improved, still are using the bee-hive oven, which conserves absolutely none of the gas, ammonia and tar. It has been definitely proved that the tremendous outlay necessary for the installation of the retort recovery ovens is more than compensated for by the prices received for the by-products or the uses to which they can be put. It is stated that the gas and coke production, provided the latter be equipped with a complete outfit of recovery plants, can together furnish tar and benzol capable of yielding annually approximately 780,000 tons of benzol, 9,600 tons of phenol, 222,000 tons of naphthalene, and 9,000 tons of anthracene; and the minor compounds, cresol, toluol, phenanthrene and carbazol in the customary relative proportions. For years, in this country, millions of gallons of benzol have been employed for enriching illuminating gas, for lack of a better market, when the enrichment could easily have been obtained from other sources. According to government reports, there are over 14,000 establishments in our country which are absolutely dependent upon dyes and colors. These establishments use over $3,000,000,000 capital, and it is estimated that over 2,000,000 men and women work in manufacturing plants which are directly dependent upon the use of artificial colors, and nearly all of these colors are made from coal-tar products.

Of course, we have taken a tremendous stride since the summer of 1914, and the conservation of coal tar and the utilization of its products are matters which have been and are dwelt upon both scientifically and commercially. The first aniline dye, mauve, was discovered by Perkin, in England, in 1856. In 1857 the industry of tar distillation was first established in this country, when Samuel Warren distilled tar in Buffalo. In 1856, likewise, magenta (previously discussed) and fuchsine were discovered. Then followed, in 1863, Hoffmann's violet and Bismarck brown; in 1864 naphthol yellow; and in 1867 the nigrosines. The manufacture of dyes was taken up with great avidity in both Germany and Switzerland. A vast amount of patient, industrious and intelligent research was expended upon the new field. France and England took up the industry with less zeal. In 1871 artificial alizarin appeared and a few years later saw chrysoidine, malachite green, eosin and a number of the current standard dyes upon the market. The United States commenced to consume great quantities of German dyes at this period, and the time was undoubtedly ripe for American enterprise. In Buffalo, in fact, in 1879, the first coal-tar dyestuff establishment was originated. About that time eight other plants went into operation and all of these depended upon European intermediates with the exception of the Buffalo works, which commenced to make aniline oil in 1884 and was forced to cease due to its inability to obtain raw materials. In 1885 only four establishments of this nature were left, and these manufactured on a mighty close margin. Incidentally, these four persevered and are flourishing at the present time. Of course, at the present time this country is manufacturing great quantities of intermediates and dyes

from its own crudes. It is estimated that the production of tar from the coke ovens and gas works of the country will probably amount to about 300,000,000 gallons at the close of 1917, which figures show the strides we have taken along these lines. The production of the 4,375,000 pounds of intermediates, which at the present time represents our monthly output, is an achievement born and grown to its present stature in two years' time. This growth is even more remarkable than that of the dyestuff industry itself, since it was well established, or fairly well, and in the hands of experienced companies years ago. At the present time we certainly are manufacturing a tremendous quantity of dyes. One concern alone, it is stated, has increased its annual output from 3,000,000 pounds to 30,000,000 pounds in the last two years. With regard to the great bulk of heavy chemicals required in the coal-tar dyestuff industry, the United States is now practically independent of the rest of the world. According to special records kept by the *Journal of Commerce*, the remarkable advance which has occurred in the dye and chemical industries of the United States in the last two years is indicated in the fact that capital authorized for new concerns in that period aggregates $186,389,000.

The following is a statement of Mr. Schoellkopf, president of the Schoellkopf Aniline and Chemical Co., which appeared in a recent issue of the *Journal of Industrial and Engineering Chemistry:* "We, as well as the other manufacturers of dyes, have been criticized for not making a greater variety of dyes. Some people seem to have an idea that it is so very simple to produce any shade or quality desired. To be perfectly frank, I think that the progress both as to quality and variety made in the last two years is truly remarkable if one considers the difficulties it has been necessary to surmount. In time and with proper encouragement the American manufacturers will produce every color that is necessary and do it just as well as our foreign competitors did it. In quality our products are absolutely identical with those imported from the other side and in some cases better. As to the *poor* quality of American dyes, the possible 100 dyes made in this country cannot do the work of the 300 or more which were formerly imported. The manufacturers do not claim they will, but many dyers try to make them do that work. The results are very bad and the dyer blames the dyes when, as a matter of fact, he knows better. For purposes of national defense it is absolutely vital that this industry should be developed. It is not just newspaper talk that dye factories can be converted into ammunition plants on short notice. It is, in fact, very reasonable since the same materials are used in producing dyes and ammunition. After the war I believe you will see the industry established in all of the warring countries and the government will, if necessary, even subsidize the manufacturers in order to keep the plants in operation."

A few weeks ago all of the newspapers came out with the startling items about Japan attempting to control the dyestuff industry of the world. This fabrication was engendered by the following news item appearing in the *Oil and Color Trade Journal:* "An enterprise has now been started in Japan under the title of the Japan Dye Manufacturing Co. So far, however, no agreement has been come to between this group and the government as to the exact interpretation of the subvention law (which fixes the subvention at 8 percent of the paid-up capital); it

has not been possible even to commence the erection of the factory building. Apparently, the project has been carelessly handled, and the great difficulties have been disregarded, as well as the question whether Japan possesses sufficient experience to enable her to take up this branch of industry and compete successfully with Germany in the dye trade after the war."

In conclusion, it might be well to attempt to answer the inquiry often raised as to why the natural resources of our country have never been utilized on any extensive scale to meet the needs of American consumers and create a distinctly American coal-tar chemical industry. The blame, I think, rests evenly upon the shoulders both of the manufacturers and the consumers. The former dwelt upon the complexities of the problem, the enormous financial outlay necessary to really progress sufficiently to meet foreign competition, and the possibility of never being able to meet this competition upon an equal basis; and so no direct attempt was ever made to focus national thought in the United States upon the problem. The latter were, as a rule, indifferent since they received dyes sufficient for their needs and perfect in every detail. And so we became dependent upon Germany and annually expended fortunes in the purchase of foreign-made materials.

What mighty changes have been wrought in the condition of this particular branch of industry in the past two years I have attempted to set forth to you in the foregoing brief summary. Miraculous, indeed, has been the upheaval, so great, in fact, that some optimists claim that by 1920 the United States will be in a position to supply itself with all materials of a chemical nature. I certainly hope that their optimism will be justified.

FROM THE LABORATORY OF THE
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THE DRUGGIST'S DUTY IN RELATION TO REGULATING AND DISPENSING EMMENAGOGUES AND VENEREAL REMEDIES.*

BY CHAS. F. KUHN, M.D.[1]

This is a subject with which we are all familiar and one that has permeated every form of human society. The proper solution of this problem will, to a great extent, elevate humanity to higher and nobler ideals in life and also avoid much unnecessary suffering and crime.

The promiscuous dispensation of drugs is a gigantic evil, the result of which is producing irreparable harm.

I am sure there are as many men of high character in the drug profession as in the practice of medicine, who could not be persuaded under any circumstance to encourage or assist in this dangerous practice, but inasmuch as the condition actually exists, I offer no apology for this paper.

Emmenagogues are remedies given for the purpose of producing menstruation. The patients applying for them, usually claim to have caught cold and express

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