

made for the results to date I must plead that about 80 per cent of the staff is now engaged on war problems, and 80 per cent of our problems are now direct war problems, and were assigned for the reason that almost all are directly in line with our previous experience.

So far the laboratory studies may be divided into five classes: (1) Processes, (2) Dye Intermediates, (3) Dyes, (4) Medicinals, (5) Analytical.

I will take these up in their order and endeavor to give a brief outline of the different kinds of experimental work that have been undertaken by the staff.

1. PROCESSES—Chlorination, sulfonation, oxidation, sublimation. All of these investigations have been for the most part vapor-phase problems.

Chlorination—Studies of a variety of compounds by means of light catalysts have been carried on. Early in our chlorination studies we found that it was impossible to interpret the results because the known analytical methods were deficient. Analytical methods for handling chlorinated toluenes have been completed, and will be published in the next issue of the *Journal of the American Chemical Society*. A technical unit for this chlorination study has been installed.

Sulfonation—These studies have involved the sulfonation of naphthalene, benzene, toluene, and some other compounds in the vapor phase by a continuous process. The analytical methods for handling the variety of derivatives of naphthalene have been completed and an article describing the sulfonation and the analysis of products is practically ready for publication. This work led to a study of methods for making H-acid, and we hope to develop results of interest on this compound.

Oxidation—Oxidation of a variety of compounds by means of catalysts have been carried on in the vapor phase. The most important development of this work is an advanced study of the manufacture of phthalic anhydride.

Sublimation—Sublimation studies have included the purification of a variety of compounds, including phthalic anhydride and a number of hydrocarbons. These studies have required the construction of the vapor pressure curves of a large number of compounds and it is hoped that these will be ready for publication shortly.

2. INTERMEDIATES—An enumeration of the dye intermediates under investigation is as follows:

Phthalic anhydride, methods of manufacture and uses.

H-acid.

A large number of sulfonic acid derivatives of naphthalene, benzene, toluene, and cymene.

The chlorine compounds of toluene and cymene and the study of a number of the quinolines.

3. DYES—*Malachite green*. A study of the Doebener process for the manufacture of malachite green led to studies on the production of benzotrichloride, and these have been included in the chlorination problems. The sulfonephthaleins, cymene dyes, dyes for sensitizing the gelatin emulsions of silver halides, and a number of dyes useful for biological purposes have been investigated.

The manufacture of a large number of compounds from cymene was made possible when the satisfactory methods for nitrating cymene were developed. A number of cymene dyes, homologues of aniline, and various aniline derivatives have been made, showing the possibility of producing as many compounds from cymene as are made from aniline.

The biological dyes have included the development of a number useful in determining the hydrogen-ion concentrations and in blood investigations. The latter are required in considerable quantity by the Surgeon General.

The sensitizing dyes are of great value in photography and are especially useful in aeronautic observation.

4. MEDICINALS—A study of the manufacture of arsphenamine and a study of the patent literature on the subject have been made, and it is hoped that the results will be ready for publication in the near future.

5. ANALYTICAL—The prosecution of many of the investigations has been dependent upon the development of analytical methods for handling the products. Analytical papers on chlorinated toluenes, oil-soluble colors for use in foods, and analysis of anthracene have been published, and other papers are in preparation. The publications that have so far appeared are as follows:

Para Cymene. I—Nitration. By C. E. ANDREWS, *THIS JOURNAL*, 10 (1918), 453.

The Use of Thymolsulfophthalein as an Indicator in Acidimetric Titrations. By A. B. CLARK AND H. A. LUBS, *J. Am. Chem. Soc.*, 40 (1918), 1443.

The Benzaldehyde Sulfite Compound as a Standard in the Quantitative Separation and Estimation of Benzaldehyde and Benzoic Acid. By G. A. GEIGER, *J. Am. Chem. Soc.*, 40 (1918), 1453.

Crystallography. Note on the Fundamental Polyhedron of the Diamond Lattice. By E. Q. ADAMS, *J. of Wash. Acad. of Sci.*, 8 (1918).

Detection of Added Color in Butter or Oleomargarine. By H. A. LUBS, *THIS JOURNAL*, 10 (1918), 436.

The Quantitative Estimation of Anthraquinone. By H. F. LEWIS, *THIS JOURNAL*, 10 (1918), 425.

A Method for the Rapid Analysis of Mixtures of Chlorinated Toluene. By H. A. LUBS AND A. B. CLARK, *J. Am. Chem. Soc.*, 40 (1918), 1449.

Plant Operations—The development of a process for the manufacture of phthalic anhydride has been studied on a plant scale. The work is carried on in coöperation with manufacturers, in accordance with the announcement of the Secretary of Agriculture published in June 1917. The experimental work is still in progress.

The chlorination of toluene on a large scale is being conducted in the technical plant of the Color Laboratory.

Plant investigations for the manufacture of various alcohols and acetone are in progress.

6. PATENTS—The results of laboratory research are patented by the inventors and dedicated to the people by the Department of Agriculture. About twelve patents have been granted and a large number of applications are pending.

The prosecution of a number of phases of this work has been due to Messrs. J. A. Ambler, R. C. Young, G. S. Bohart, and L. E. Wise, in addition to those who have already been listed as publishing articles from this laboratory.

PROBLEMS IN TESTING DYES AND INTERMEDIATES

By E. W. PIERCE, of the U. S. Conditioning and Testing Company

The purpose of this paper is not to disclose any new developments along the lines of dye testing, but rather to make a plea for general coöperation in order to raise the subject to the level it should occupy, now that we have the initiative.

Having been in the most intimate contact with dye testing from an American point of view, for a period of over 20 years, I feel that whatever criticisms I may make are at the same time retroactive.

It cannot be denied that all the present methods of testing dyestuffs are empiric and subject to a wide limit of error. For commercial purposes no great objection is made if this error is plus or minus 2.5 per cent, that is, regarding tinctorial power only. No attempt has been made so far in the valuation of dyes which would take into account the presence or absence of small quantities of by-products or impurities that might be less than 1 per cent and yet cause a marked loss in value of the commercial dye. Thus some recent productions of Rhodamine B were made almost valueless by the presence of a very small quantity of an impurity which caused the shade to be flat and useless for dyeing pinks. A chemical analysis of such a product

might show it to be 99 per cent pure, well within the commercial allowance, but it is still much inferior to a lot that would analyze 90 per cent Rhodamine and 10 per cent dextrine and capable of dyeing a bright shade.

According to the ultimate uses of the dyes, tests are made in a manner that aims to duplicate, on a small scale, the actual application of the color. Dyeings on wool, cotton, and silk, the most common, are followed by paper pulp, lakes, leather, sugar, starch, etc. Colorimetric methods are more recent, but have many limitations.

If it were always possible to obtain identical conditions in the comparative dye test, the only source of error would be that of the individual's ability to read results accurately. However, the dye test has shown that many influences, apparently insignificant, are capable of causing misleading results.

The water used in dyeing is a well-known factor, differences of over 10 per cent being noted between filtered river water and distilled water. Dyes that are equal when tested by one observer may show a difference when tested by another on account of this condition. The presence of foreign material such as salt, Glauber salt, dextrine, or soluble starch may influence greatly the result of tests by two different laboratories. The salts generally act as precipitants and cause both superficial dyeing and lake formation in the dye bath, while the presence of the organic adulterants is like that of a protective colloid and results in slower dyeing, a less exhausted bath, and a greater penetration of the fiber. When the dye bath is finally exhausted, the appearance of the skein in both cases may be satisfactory to the naked eye, but the microscope will show that the one with the dye on the surface of the fiber has a false advantage.

The fibers themselves are not of a nature that would recommend them for exact scientific work. A wool fiber invariably dyes a very full and often bronzy shade near the tip, then becomes lighter toward the root, while the root end is often left practically unstained. The carding and spinning processes so mix the fibers that the naked eye does not notice these defects in a skein or piece of cloth, but they exist and the final result is modified accordingly. When the dye bath contains materials that influence the evenness of the individual fiber the dyeing as a whole shows the effect. These materials may be either actual impurities or placed there intentionally.

Silks are not uniform but are classed as hard- and soft-natured and accordingly dye superficially or uniformly.

Mordanted skeins may be the source of many differences between different observers. The tannin-antimony mordant on cotton is at times a true colloidal adsorption between cellulose and antimony tannate and at others a mechanical adhesion of the antimony compound on the surface of the fiber. The acidity of the dye bath removes and again deposits the final combination with the dye so that the most rigid maintenance of uniform conditions is necessary to obtain concordant results.

Lately a test of hemates by the method of non-oxidizing mordants was required in a hurry, and as no mordanted skeins were on hand they were prepared as usual and the dyeings followed at once. As the results were not satisfactory the test was repeated on the following day with mordanted skeins from the same lot. The second test showed almost double the amount of color of the first series, and the conclusion has been forced upon us that a chrome mordant on wool improves by ageing for 12 hours before use. Failure to observe this condition might result in discrepancies hard to explain.

The most satisfactory test of dyestuff strength is by the colorimeter, but such methods are only dependable when the two solutions are identical in composition and shade. Any variation in acidity, alkalinity, or tone of the color detract from accuracy. It is particularly noticeable now that the productions of different factories vary just enough to interfere with the use of the colorimeter, although it will be found most valuable in controlling the output of any plant.

A few words may be said on the subject of intermediates. It is vitally necessary that some authoritative body specify tests for the proper valuation of the common intermediates. The literature on the subjects is insufficient. Take the case of paraphenylene diamine. We can determine ash, nitrogen, melting and boiling point, solubility, and so on, but these are not a true indication of its suitability for dyestuff manufacture. The presence of isomeric bodies is the greatest fault and none of the ordinary tests are quantitative. It cannot be hoped that we will ever have a system of quantitative methods for aromatic compounds but some of the gaps may be filled. At times it is possible to convert an intermediate into a distinctive coloring matter and make a colorimetric comparison with a sample of the C. P. product and so far this has been the best method at hand.

Isolated cases like paranitraniline have given special methods, such as titration in boiling solution with sodium nitrate, using safranin as an indicator, but whenever there is a tendency to develop a strong color this method is valueless.

If we are now to make America the center of the dye industry it is incumbent upon us to provide the analyst with methods and so facilitate the commercial development along proper lines of control.

ON THE QUANTITATIVE ANALYSIS OF DYESTUFFS

By ALFRED H. HALLAND, of National Aniline and Chemical Company

The large majority of commercial dyestuffs contains besides the dyestuff proper a certain amount of moisture and a great variety of inert ingredients such as common salt, sulfate of soda, carbonate of soda, etc. While a certain amount of these bodies frequently are added in the process known as "Standardization," it is well known that it is practically impossible to isolate water-soluble dyestuffs without a minimum amount of salt, sulfate, and, to a lesser degree, sodium carbonate.

By the quantitative examination of a dyestuff I understand the determination of these various ingredients as well as of the coloring matter proper.

Before going into details I venture to state as my personal opinion that this line of work is being neglected in most dyestuff factories. When a manufacturing chemist delivers a quantity of dye to be "Standardized" he is too often satisfied if said quantity yields a fair amount of "Type." Am I much mistaken when I say that the chemist in many cases does not know what this "Type" really consists of? A quantitative analysis of each of his "Types" would show the chemist just what degree of perfection his manufacturing process has reached. It would either give him the satisfaction of knowing that his process was good or be an incentive to him to improve it. In the case of a great many complex dyestuffs, for example, certain polyazo dyestuffs, the actual yield of dyestuff from given quantities of intermediates is really quite poor. A quantitative analysis of the finished dyestuff, as well as of the intermediate azo bodies, should be instructive and should be carried out in all cases of bad yields. It would obviously only be necessary to do this work once for each individual "Type" as all future lots could be compared to the "Type" by the usual dyeing tests.

The quantitative determination of sulfur present as sulfonic acid groups, or of the degree of saturation of these with soda or potash, or of halogen, if such be present in the molecule, would form a valuable addition to the knowledge gained by a purely qualitative analysis of dyestuffs such as the chemist is occasionally called upon to make.

I now would like to review the methods which we have used in Buffalo with a fair degree of success. While I do not claim any scientific perfection or absolute accuracy for them, they have not been found seriously wanting.

DETERMINATION OF MOISTURE

Certain water-insoluble dyestuffs such as oil-soluble azo dyes, lake colors, bromo acid, etc., contain none, or very little moisture.