possible at this time to secure a very satisfactory grade of methyl orange. It is recommended that purchasers specify methyl orange of a grade to be used as an indicator and also stipulate that the insoluble residue from one gram dissolved in 400 cc. of water shall not exceed 0.025 g.

III—SULFURIC ACID FREE FROM NITRATE: THE DIPHENYLAMINE TEST FOR NITRATES¹

The diphenylamine test for nitrate has been studied carefully by J. Tillmans,² who reviews previous work and describes the best conditions for making the test. The most satisfactory reagent is prepared by dissolving 0.017 g. of diphenylamine in 100 cc. of concentrated sulfuric acid (sp. gr. 1.84), and adding 30 cc. of water.

At a time when there was no sulfuric acid in the Bureau of Chemistry which would give a colorless reagent, four producers and dealers were asked whether they could furnish such acid. Dealer A stated that they had never handled acid which would give absolutely no color under the conditions described, but that one grade furnished by Maker C was the nearest this quality which they had received. Producer B stated that they could not furnish acid which would not give a trace of green color, but at a later date stated that they were then able to furnish the required acid on request. Producer C stated that they could furnish such acid if reference was made to their letter on the subject. This acid proved perfectly satisfactory for making the reagent. Producer D stated that all their acid was of the quality desired. One bottle was ordered for examination. The blue color developed on making the reagent was darker than was obtained with any of the samples of acid on hand in the Bureau, and the acid was returned to the dealer.

This experience shows that sulfuric acid can be secured which will serve for preparing the diphenylamine reagent, but this grade must be specified clearly, and purchased subject to examination.

The very low limits for sensitiveness reached by Tillmans were not found in the tests for nitrates in sulfuric acid. He and others have pointed out the number of other substances which produce the blue color. It must be understood that a positive test does not prove the presence of nitrates, but a negative

result shows the absence of the minimum quantity necessary to give a test.

METHOD OF NITRATE TEST

A number of methods of applying the diphenylamine test were tried in order to select one which would serve to assure sulfuric acid sufficiently free from nitrates for careful analytical work without making the test too exacting. The U. S. Pharmacopeia test prescribes mixing the acid with nine volumes of water and pouring the mixture carefully over a reagent made with 0.5 g. of diphenylamine dissolved in 100 cc. of sulfuric acid and 20 cc. of water. Sulfuric acid containing 0.02 per cent N_2O_5 gives a blue ring at the place of contact of the two layers. Acid with 0.01 per cent N_2O_5 gives no color.

A simple application of the test is to add a drop or two of the U. S. Pharmacopeia reagent to 3 to 5 cc. of the acid in a test tube and overlay with water. A blue ring develops in 10 min. if the acid contains 0.00002 per cent of N_2O_5 . With 0.00001 per cent the ring is seen in some instances and not in others.

When 2 cc. of sulfuric acid are mixed with 1 cc. of water and there are added immediately to the mixture 1 cc. of reagent made with 0.017 g. diphenylamine, 100 cc. of sulfuric acid (sp. gr. 1.84), and 30 cc. of water, a decided blue color develops in 10 min. if the acid contains 0.00005 per cent N_2O_5 . If the mixture of acid and water is cooled to 20° C. before addition of the reagent, no blue color is developed in 10 min. if the acid contains less than 0.0001 per cent N_2O_5 . Nearly all the reagent sulfuric acid on the market will pass this test.

The presence of too large a quantity of diphenylamine interferes with the test. Increasing the proportion of either water or sulfuric acid in the reagent as described by Tillmans makes the test less sensitive. The preparation of the reagent is thus the most delicate test for the presence of nitrates, nitrites, or some of the other substances which give the blue color with diphenylamine. Sulfuric acid containing 0.000008 per cent N_2O_5 shows a decided faint blue color in 2 hrs. after preparing the reagent. Acid with less nitric present will serve to prepare a reagent which will be perfectly colorless.

Acid of this grade can be purchased if it is specified that this test must be met.

ADDRESSES AND CONTRIBUTED ARTICLES

CERTAIN ASPECTS OF THE CHEMISTRY OF CELLULOSE ACETATE FROM THE COLLOIDAL VIEWPOINT¹

By Gustavus J. Esselen, Jr.

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If one were asked for a good example of a colloidal solution in a non-aqueous solvent, probably among the first materials to come to mind would be solutions of cellulose esters. In spite of this, it is only comparatively recently that the colloidal character of the parent substance cellulose has been recognized.

¹ Read at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

Harrison¹ has correlated in a most interesting manner many of the reactions of cellulose, as, for example, its behavior when treated with alkalies, acids or oxidizing agents, by considering the typical cellulose, cotton, as existing in a number of different degrees of colloidal dispersion. Cross² has also referred to cellulose as a colloid, and Miss Minor³ has recently considered the hydration of cellulose in paper making from the standpoint of colloid chemistry. Whether or not the solution of the prob-

¹ *Trans. Nat. Assoc. Cotton Mfrs.*, **101** (1916), 201. 2nd Report on Colloid Chem., Brit. Assn. Adv. Sci., **1918**, 52.

² *J. Soc. Dyers Colourists*, **34** (1918), 92.

³ *Paper*, **25** (1919), 700.

lem of the constitution of the cellulose molecule is ultimately to be found in these colloidal considerations, the point of view which they present is certainly helpful in correlating many previously unconnected observations. Once it is admitted that cellulose is a colloid, all its transformations are to be considered as colloid chemical processes and as such involve one or more of the various phenomena, such as adsorption, change in degree of dispersion, etc., which we have come to associate with materials in the colloidal state.

This is not the place, nor is there time, to discuss at any length the underlying principles of colloid chemistry. There is, however, one phase of the matter which it is well to keep constantly in mind, and that is, that in substances dispersed colloiddally the surface is unusually great in proportion to the mass. This being so, we should expect all surface phenomena to be emphasized. We shall have special occasion to refer to the particular surface phenomenon of adsorption, which Langmuir¹ considers to be intimately connected with the time lag between the striking of an ion or molecule on a surface and the rebounding from that surface. This gives a picture of the process which helps to fix in the mind some of the particular steps which are referred to later. Miss Minor² has pointed out that where cellulose is under consideration, another of Langmuir's postulates also seems to have particular significance: that is, his definition of a colloid molecule as a large aggregate of atoms or group molecules held together by secondary valence.

CATALYTIC ACTION OF SULFURIC ACID

In its simplest terms, cellulose acetate is formed by the esterification of cellulose by means of acetic anhydride in the presence of a catalyst. There are two general methods of producing cellulose acetate, both of which have a number of variations. One results in a fibrous acetate resembling in outward appearance the original cotton used as raw material; the other gives a granular product. In all methods the most common catalyst is sulfuric acid dissolved in acetic acid, which acts as a carrier. In some instances the cellulose is first given a preliminary treatment with the mixture of sulfuric and acetic acids, sometimes in the presence of a little water. The treatment is often referred to as a hydration, but its exact nature has not been established. Whether or not a preliminary treatment is given before adding the acetic anhydride, the sulfuric acid is adsorbed by the cellulose from the solution. These sulfuric acid-cellulose compounds were at one time considered to be true molecular compounds, but they are now recognized as adsorption compounds, forming a series in which the percentage of sulfuric acid varies by much more gradual changes than could be accounted for on the basis of simple molecular proportions. This either results in, or is accompanied by a swelling and peptization of the cellulose to an extent depending upon the temperature and time. As indications that the degree of dispersion is really modified, there may be cited the observations that the longer the preliminary treatment, the more rapid the subsequent esterification and the less viscous the solutions of the product. The success of the process is doubtless due quite as much to the modification of the colloidal state of the cellulose as to the usual effect of the catalyst in facilitating esterification. In this latter connection it may be noted that because of being right on the surface where the reaction must take place, the catalyst is in a peculiarly effective situation for promoting the esterification.

In making the granular form of cellulose acetate, cellulose, usually in the form of cotton, is treated with a mixture of acetic acid, acetic anhydride, and a suitable catalyst. The acetic acid acts merely as a carrier and takes no part in the reaction. As mentioned above, the catalyst dissolved in acetic acid is frequently mixed with the cellulose some time before the anhy-

dride is added, although in other cases all are added together. Since cellulose acetate is soluble in acetic acid, the cellulose dissolves as the esterification proceeds. Samples are taken from time to time and when the desired solubility has been attained, the reaction is stopped by adding an excess of water which destroys any remaining anhydride and precipitates the cellulose acetate. In the earlier processes, the acetate thus formed was the tri-acetate corresponding to the hexanitrate. It later developed¹ that owing to their wider range of solubility the acetates of most technical usefulness were those with a somewhat lower acetyl content than would correspond to a hexa-acetate on the C_{12} basis, but higher than would correspond to a penta-acetate. These were at first prepared by adding small and carefully regulated amounts of water and sulfuric acid to the solution of cellulose acetate in acetic acid. As before, when the desired solubility was attained, the product was isolated by precipitation with water. While outwardly this secondary treatment is one of partial saponification, it is actually much more intimately connected with the colloid properties of the cellulose acetate. The reason for this statement is that an equivalent degree of saponification obtained by methods not involving the solution of the acetate does not give a product with the same wide range of solubilities. The effect may very possibly be connected with the opening up of the molecule in such a way as to make the $-CO$ group more reactive, because it results in a greatly increased solubility in acetone.

In preparing cellulose acetate in fibrous form, it is given a preliminary treatment with sulfuric acid dissolved in glacial acetic acid, this step being similar to the one for preparing granular cellulose acetate. After removing the surplus preliminary bath in a centrifuge or press, the cellulose is immersed in a mixture of acetic acid, acetic anhydride, and some non-solvent hydrocarbon like kerosene, or benzene. While the proportion of non-solvent is so regulated that the cellulose acetate does not dissolve, the conversion is accompanied by a marked swelling and by a noticeable change in the index of refraction. When the product has reached the desired degree of solubility, the surplus bath is removed, and the residue thoroughly washed with water. The product is cellulose tri-acetate, which is subjected to a partial saponification to render it soluble in acetone.

CELLULOSE ACETATE SOLVENTS

One of the earliest solvents for cellulose acetate was chloroform, and it was soon noticed that solutions in this solvent were markedly improved by the addition of small amounts of alcohol. The improvement in solubility passes through a maximum and then gradually falls off until finally a proportion of alcohol is reached which gives a mixture with chloroform in which cellulose acetate is no longer soluble. So far as I know, no explanation has ever been offered for this behavior. A possible explanation may be found if we remember that cellulose and its compounds have marked affinity for hydroxyl groups. In fact, if the size of the negative charge² assumed when immersed in water is a reliable criterion, cellulose acetate has a considerably greater affinity for hydroxyl groups than cellulose has. When alcohol is added to a chloroform solution, it may be that the cellulose acetate adsorbs the alcohol, in which case the hydroxyl groups would probably be next the cellulose acetate, and the hydrocarbon radicals would be sticking out into the solution. Reasoning from the analogous effect of a dilute sodium hydroxide solution on cellulose, a slight swelling of the cellulose acetate might well be assumed with the possibility of an accompanying increase in dispersion. This may be one of the effects entering into the improvement in solubility when alcohol is added. A second effect may be that the hydrocarbon groups exert more of an attraction on the hydrocarbon end of the chloroform molecule than

¹ *J. Am. Chem. Soc.*, **36** (1914), 2221; **39** (1917), 1849.

² *Loc. cit.*

¹ *Ost, Z. angew. Chem.*, **32** (1919), 66, 76, 82; *Chem. Abs.*, **13** (1919), 2760.

² *Trans. Nat. Assoc. Cotton Mfgs.*, **101** (1916), 218.

does cellulose acetate itself, which would also tend to improve the solubility. The maximum point in the curve may correspond to the point at which all the secondary valences of the surface of the cellulose acetate are just saturated with alcohol. Since the cellulose acetate is in a colloidal degree of dispersion, its surface will be large and a considerable amount of alcohol will be required. In practice, this point is reached when alcohol constitutes about 25 to 30 per cent of the solvent mixture. Inasmuch as alcohol is not itself a solvent for the usual forms of cellulose acetate, any more than dilute caustic soda solutions are solvents for cellulose, it is natural that further additions of alcohol should gradually tend toward making the mixture a non-solvent. There is a further analogy between the action of dilute caustic soda solution on cellulose and that of alcohol on cellulose acetate, in that certain forms of cellulose acetate are known which are soluble in hot alcohol, corresponding to those forms of cellulose precipitated from zinc chloride or cuprammonium solutions, which are soluble in aqueous alkalis.

Another interesting example of the beneficial effect of alcohol is in connection with aromatic hydrocarbons. Cellulose acetate is not soluble in benzene either at room temperature or at the boiling temperature. However, if a certain amount of alcohol is added to the benzene, the mixture becomes a solvent for the cellulose acetate when warmed. This is true even with those varieties of cellulose acetate which are not soluble in hot alcohol. Here again, we may have the same explanation as in the previous instance, *i. e.*, the alcohol may be adsorbed and the hydrocarbon radicals may be sufficiently attracted by the benzene to cause the cellulose acetate with its adsorbed alcohol to go into solution.

One might, at first sight, think that if this proposed theory were correct, mixtures of aliphatic hydrocarbons and alcohol should also be expected to act as solvents for cellulose acetate, which is not the case. On further consideration it will be seen that the fact that aliphatic hydrocarbons and alcohol are not solvents for cellulose acetate is merely another piece of evidence that the theory is really the true explanation. From the fact that heat is required to effect the solution of cellulose acetate in mixtures of benzene and alcohol, we may conclude that the attraction between the adsorbed alcohol and the benzene is very near the minimum amount required for solution. If the attraction were very much less, we should not get the resulting solubility. Now we know that benzene has much more of an attraction for alcohol than have the aliphatic hydrocarbons ordinarily met with in petroleum solvents such as gasoline or kerosene. These relative attractions are well illustrated by the fact that kerosene and gasoline are not miscible with ethyl alcohol, except in very small proportions, whereas alcohol and benzene are readily miscible. Therefore, since the attraction between benzene and alcohol is just about the minimum necessary to bring the cellulose acetate into solution, and since the attraction between alcohol and the ordinary aliphatic hydrocarbons is distinctly less, it is not to be expected, if the proposed theory is correct, that the latter mixtures would be solvents of cellulose acetate. It is seen, therefore, that the solubility in alcohol and chloroform is intimately connected with the solubility in alcohol and benzene.

As an outcome of this consideration of the reason for the solubility of cellulose acetate in mixtures of benzene and alcohol, it would naturally be expected that if the theory held true, such materials as combined an aromatic radical and a hydroxyl group in one molecule should also be solvents for cellulose acetate. This is known to be true, since the phenols as a class are among the very best solvents for cellulose acetate.

To sum up, it is pointed out that it is not unreasonable to expect that when ethyl or methyl alcohol is added to a chloroform solution of cellulose acetate, the alcohol is adsorbed by the colloidal cellulose acetate, the hydroxyl groups probably being

nearest the surface of the cellulose acetate particles. The resulting improvement in solubility which occurs may then be explained as due to a combination of two effects: first, a swelling and possible increase in the degree of dispersion of the cellulose acetate; and second, a greater attraction for the chloroform by the simple hydrocarbon radical of the alcohol than by the more complex cellulose acetate. The theory is extended to explain the solubility of cellulose acetate in mixtures of alcohol and benzene and in phenols, which, as a class, are excellent solvents for cellulose acetate.

There are, then, two classes of solvents for cellulose acetate whose solvent properties may be, to a certain extent, at least, explained. In the first class are those solvents like acetic acid, ethyl acetate, and triacetin which contain acetyl groups and whose solvent action is to be explained on the ground that they are presumably of the same general type as cellulose acetate. In the second class are certain compounds and mixtures containing hydroxyl groups combined with aromatic or certain of the simpler aliphatic hydrocarbon radicals, the solvent action of which has been explained above.

It is recognized that there are still other solvents of cellulose acetate which are not included in either of the above general divisions, and it is hoped that a correlation can later be made of many of the observed phenomena in these instances also.

CHEMICAL CONTROL IN THE BEET SUGAR INDUSTRY¹

By S. J. Osborn

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The chemical control of a beet sugar factory may range from almost nothing up to the work performed by a large and highly complex organization. It is the purpose of this paper to give some idea of the activities of a chemical department of the latter type.

The beet sugar chemist was formerly a poorly paid individual who was expected to do a certain amount of laboratory work with the help of perhaps one or two assistants. He was frequently a man of very limited technical education, and, owing to the fact that a beet sugar factory operates for only three or four months during the year, the chemist was often considered of not sufficient importance to be kept on the payroll after the end of the campaign, or operating season. Naturally this did not conduce to the development of a high grade of work or to the standing of the chemist in the industry.

In some companies of sufficient size the chemical control work is now handled by a specially organized chemical department, entirely independent of the operating department, although the two naturally enjoy intimate relations and must work in close coöperation to achieve the best results. This system has many advantages. Not only does it relieve the operating department of responsibility for a highly technical line of work, but it puts the results on a basis where they are free from even any suspicion of bias or irregularity, and facilitates the introduction and use of uniform methods of analysis and control at all factories of the organization. Naturally it does not pay to develop an elaborate system of chemical control unless the operating and engineering departments are also sufficiently developed to use and apply the data, and the growth of the several departments will therefore go hand in hand.

METHODS OF CHEMICAL CONTROL

While the beet sugar manufacturing process is not a highly complicated one, as chemical processes go, it is doubtful if any other manufacturing process is so closely and thoroughly controlled at every step by the chemical laboratory.

An important factor in the development and application of chemical control in all branches of the sugar industry is the

¹ Read at the 59th Meeting before the Sugar Section of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.