(Compare tests 62 and 58, 63 and 59, 64 and 60, and 65 and 61.) Figure 7 shows the percentages of sulfur in the cokes and the percentages of coal sulfur retained in the cokes plotted against hours of heating at 800° C. for both the 4-hour and the 5-hour series of tests. By subtracting the plotted hours of heating, from 4 or 5 hours, depending on the test series, the corresponding times of heating at 500° C., as given in Table X, are obtained.

ACKNOWLEDGMENT

The authors are indebted to H. M. Cooper and R. F. Abernethy, under whose supervision all analyses of the coal, coke, and tar samples were made, and to D. A. Reynolds for valuable suggestions in the preparation of the manuscript.

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Vapor Phase Condensation of Aniline to Diphenylamine

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The vapor phase condensation of aniline to diphenylamine and ammonia is shown to take place in good yield over activated alumina. Under optimum conditions no detectable amount of side reaction or decomposition occurs. The conversion per pass increases with decreasing space velocity and increasing temperature, appreciable reaction beginning at temperatures above 400° C. The optimum temperature is 460° C.; above this, decomposition of the aniline and diphenylamine takes place, resulting in a darkened product and loss of the unreacted aniline. The maximum conversion in the equipment used was approximately 35%, the average being between 20 and 25%. Under optimum conditions, because of the absence of side reactions, yields after recycling should approach the theoretical. It is concluded from the thermodynamics of the reaction that industrial-sized equipment would increase the per pass conversion considerably since the reaction seems entirely dependent on rate factors. It is thought that with the possible recycle of the unreacted aniline, the high purity of product obtainable by this process, and the other characteristics described herein, the process is of possible industrial interest.

ALTHOUGH diphenylamine was known to the chemist as early as 1900, and was manufactured in Europe by the Badische Aniline and Soda Fabrik only a few years later, its commercial manufacture in this country was not undertaken until 1916. Flurscheim developed the process (*4*) and assigned his patent to Du Pont, which undertook production initially to satisfy the wartime need for an antioxidant to be incorporated in smokeless powders, cellulose base explosives, and other nitration process explosives. In this role it is termed a stabilizer. Since this time several of the diphenylamine derivatives have entered the field and are somewhat more successful. Among these, the following are most widely used:

p-Isopropoxydiphenylamine
Mono- and diheptyldiphenylamine
p-Hydroxydiphenylamine
p-Allyloxydiphenylamine
p-Aminohydroxydiphenylamine

The use of these compounds as antioxidants has spread to the synthetic rubber and plastics industry where their purpose and use is much the same.

Other important uses of diphenylamine include dye manufacture, in which it is the starting material for at least two large classes, and is considered the parent substance for some 28 commercially available types; perfume manufacture in which certain of the intermediates are diphenylamine based; the manufacture of adamsite, a war gas; the manufacture of addition agents for metal finishing; and the manufacture of many other chemical intermediates within the organic industries.

Since the Flurscheim patent in 1917 many different reactions have been proposed for the production of diphenylamine. They have all been similar, however, in that a mixture of aniline, aniline-mineral acid salt, and catalyst were to be refluxed for 10 to 30 hours, depending somewhat on the pressure proposed. The catalysts have invariably been metal halides. A complete history of this development is available in the chemical literature.

As an illustrative example of liquid phase commercial operation, the patents of Frei (*5*) in 1932, Acken (*1, 2*) in 1937–38, and Wester, Burrows, and Johnson (*11*) in 1948, all assigned to Du Pont, may be cited. The Frei-Acken process involved the use of aniline and aniline hydrochloride in the presence of zinc chloride. Operating pressures were of the order of 20 atmospheres, and the mixture was refluxed for 8 to 10 hours, at temperatures above 300° C. Conversions were reported to be around 40%, with the product being recovered by vacuum distillation. The amount of side reaction and aniline loss is not indicated.

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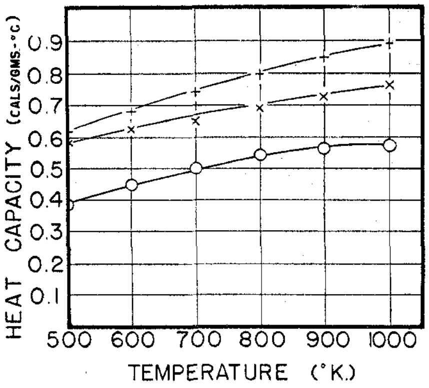


Figure 1. Heat Capacity-Temperature Curves for Diphenylamine, Aniline, and Ammonia Vapor State

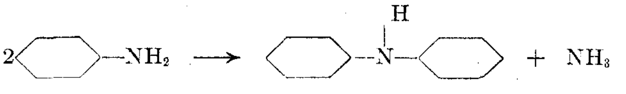
○. Diphenylamine
+. Aniline
×. Ammonia

Improved conversions are claimed for the method represented by the patent of Wester, Burrows, and Johnson (*11*). This method consists of a reaction involving only aniline in the presence of a more active catalyst, ferric chloride, in iron autoclaves under superatmospheric pressures and at elevated temperatures. The pressure range cited varies from 350 pounds per square inch to as low as 100 pounds per square inch. Reaction times of 8.5 to 20 hours produced conversions of 38 to 59%, requiring catalysts in the range of 0.3 to 8%. No information is given as to the extent of side reactions and aniline loss.

In comparison with the above, a vapor phase process involving only the passage of aniline vapor through a catalyst bed to give the desired reaction appeared to have several advantages. It was felt that the possibilities of better yields (although possibly not better conversions), better control of reaction conditions, and possibly an initially purer product were sufficient justification for investigating the vapor phase method.

THERMODYNAMIC STUDIES

The reaction thermodynamics of a vapor phase system for the manufacture of diphenylamine from aniline according to the following equation:



were considered. It was found that the reaction should be exothermic, the heat of reaction increasing from −7000 calories per mole at 600° K. to −25,000 calories per mole at 1000° K. Since little thermophysical data are available for either aniline or diphenylamine, much of that required was calculated from fundamental considerations. The heat of reaction at 25° C. was obtained from bond energies and the resonance energy change (*10*). The heat capacity–temperature relationship was calculated from the equations developed by Dobratz from original work by Bennewitz and Rossner (*3*). The equilibrium constant was calculated and found to be extremely large, approximately 10^{28} over the temperature range of interest; thus, the reaction was considered to be dependent only on kinetic factors. Assuming a simple gas phase, homogeneous, bimolecular collision, the value of the reaction rate constant also appeared quite favorable ($\log k = -4$ at 500° K., 4.1 at 1000° K. in cubic centimeters per mole per second). These values indicate only that even under such adverse conditions as a noncatalyzed reaction, the rate appears favorable. Furthermore, admittedly the means whereby these values were estimated are far from exact, and the resulting figures are only approximate in the fullest sense of the word.

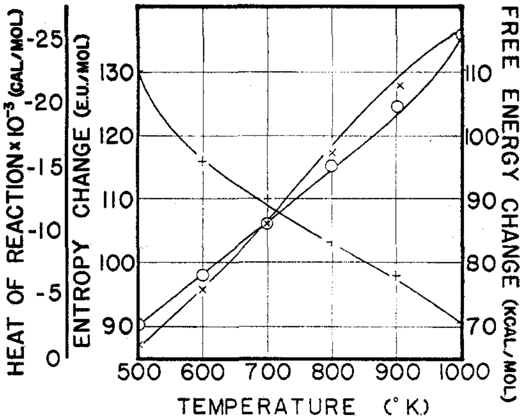


Figure 2. Variation in Heat of Reaction, Entropy Change, and Free Energy Change with Temperature

○. ΔF *vs.* T
×. ΔH *vs.* T
+. ΔS *vs.* T

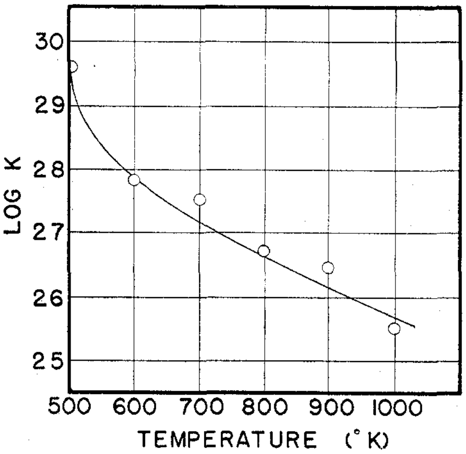


Figure 3. Variation of Equilibrium Constant with Temperature

A summary of thermodynamic and kinetic data is given in Table I, with corresponding reference equations. Heat capacity–temperature data are plotted in Figure 1; heat of reaction, entropy change, and free energy change with temperature are shown in Figure 2; and the relationship between temperature and the equilibrium constant is given in Figure 3.

APPARATUS

The apparatus used consisted essentially of three component parts, the liquid feed system and vaporizer, the reaction chamber, and the condensing and separating system. Liquid aniline was fed at a constant rate to a flash vaporizer, and the vapors, in an atmosphere of nitrogen, passed through the reaction chamber, and then to the condensing and separating unit. The generalized flow diagram, details and materials of construction, and the dimensions of the individual pieces of apparatus used are shown in the accompanying diagrams, Figures 4, 5, and 6.

The rate of feed to the vaporizer, Figure 5, was controlled by means of a capillary tube located as shown in Figure 4. These tubes were available in several sizes and could be easily exchanged prior to a run to give a desired feed rate. Feeds ranging from approximately 5 grams per minute to 30 grams per minute were possible, this range being entirely satisfactory from the standpoint of the vaporizer capacity. The initial work was done in a jacketed reaction chamber of twice the inside diameter but of the same length as the one described herein. Both Aröchlor 1248 and mercury were refluxed separately in the jacket as a heat transfer medium. After considerable preliminary work, it was found that the simple Nichrome wound-electrically heated chamber, Figure

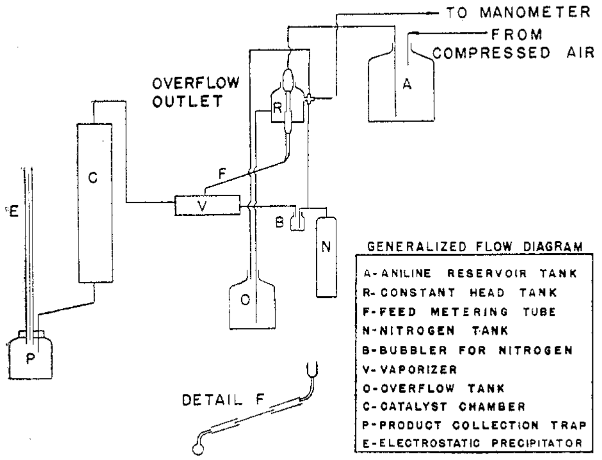


Figure 4

6, was far more satisfactory. The permissible range of temperatures was much broader and the accuracy of temperature control much greater. Variations of only ±3 degrees across the 4-foot length of chamber were easily obtained with the direct electrically heated unit, whereas 10- to 30-degree variations were common with the jacketed chamber.

Temperature measurement was accomplished by means of iron-constantan thermocouples located in the central thermocouple well as shown. Millivoltages were recorded continuously by an 8-point, custom-made, Speedomax G, variable-range, Leeds & Northrup recorder, having a sweep time of 30 seconds.

The chamber effluent was passed through an air-cooled condenser as shown, the liquid product collected, and the noncondensable gases vented. For the case of high aniline feed rates, or low nitrogen feed rates, a fog or mist resulted which was found to be extremely difficult to handle. Condensation at low temperatures, trapping through beds of glass beads, wool, or rings, and bubbling through liquid aniline were tried without success in breaking the fog formation. Finally, the electrostatic precipitator shown in the diagram, Figure 4, was constructed. The precipitator was constructed of a 1.25-inch inside diameter glass tube wound with Nichrome wire around the outside. This constituted one of the two electrodes, the other being a centrally located metallic rod. Across the two electrodes was impressed the output of a Ford Model T spark coil, driven by a 6-volt storage battery. This unit was found to be entirely successful in separating the mist from the nitrogen carrier.

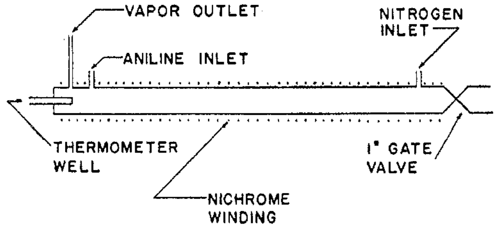


Figure 5. Details of Vaporizer

Length, 18 inches; inside diameter, 1 inch; stainless steel construction insulated with asbestos tape

SUMMARY OF EXPERIMENTATION

The experimental work was divided into two sections, the first designed to discover a material which could be shown to possess activity in promoting the desired reaction, the second designed to discover the optimum operating conditions with such a catalyst. The literature was searched to find those substances which could possibly catalyze the desired reaction. Selection was made on the basis of demonstrated activity with regard to the carbon-nitrogen bond and the hydrogen-nitrogen bond. The following list of catalyst materials were thoroughly investigated:

Titanox
Cadmium sulfide
Zinc chloride
Copper oxide
Chromic oxide
Copper chromite
Nickelic oxide
Haber-type catalyst (unreduced)
Haber-type catalyst (reduced with hydrogen prior to use)
Alumina cylinders
Activated alumina, Alcoa *F* series (crystalline)
Activated alumina, Alcoa *H* series (gel-type)

The alumina cylinders were generally used as the support, and the other materials impregnated on them. In only three cases was this not done; the Haber catalyst and the activated aluminas, being already sufficiently pelletized, were used as received. Mesh sizes of 8 to 14 mesh and 4 to 8 mesh were studied in these latter materials. The support cylinders were prepared by the Norton Company, Worcester, Mass.; their designation was LA-103E-16. The diameter of these cylinders was equal to their length, and they were available in $^1/_4$, $^3/_{16}$, and $^1/_8$-inch sizes. All three sizes were used during the course of the investigation, after it was first established that the alumina in that form had no activity.

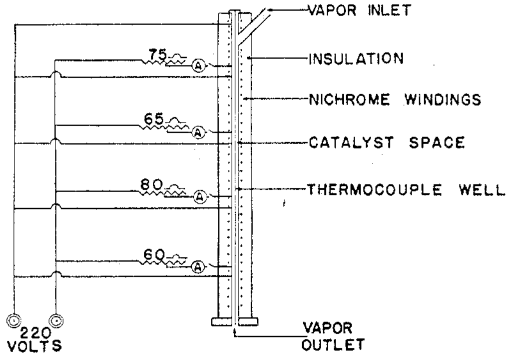


Figure 6. Details of Catalyst Chamber

Stainless steel; 580-cc. volume

Conversion and, correspondingly, catalyst activity was shown to exist in only three of the above list of materials. The copper chromite and the activated aluminas are catalysts for the desired reaction. The chromite catalyst, however, produced large amounts of side reaction, and decomposition and oxidation of the diphenylamine and aniline were so extensive as to make this material of little further use. The activated aluminas, on the other hand, under optimum conditions, catalyzed only the desired reaction and no others, producing an effluent composed only of aniline and diphenylamine. White crystals of the latter material were obtained as a precipitate from solutions of the effluent in concentrated hydrochloric acid by dilution, the diphenylamine being insoluble in acids below 6 *N* concentration. Furthermore, the aniline, in any sample, could be effectively removed by simple vacuum distillation and was always found to be identical in color with the feed material. After several condensation runs made under optimum conditions, the theory amount of aniline was removed or accounted for, within the limits of experimental error. The diphenylamine remained behind and crystallized in the distillation flask. Industrially, a partial condenser could remove the diphenylamine as a liquid leaving the aniline in the vapor state for recycle immediately. The melting point of the diphenylamine as recovered by either of the methods described consistently varied between 51° to 53° C., comparing favorably with the literature value of 52.9° C. The production of the dye, diphenylamine blue, in every case qualitatively verified the presence of diphenylamine.

Table I. Thermodynamic and Kinetic Data

Variable	Compound	State	Reference Equation	Unit	T, ° K. 500	600	700	800	900	1000
C_p	Diphenylamine	Vapor	1	Cal./gram/° C.	0.39	0.45	0.50	0.54	0.56	0.57
C_p	Aniline	Vapor	2	Cal./gram/° C.	0.60	0.68	0.74	0.80	0.85	0.89
C_p	Ammonia	Vapor	3	Cal./gram/° C.	0.58	0.62	0.65	0.69	0.73	0.77
ΔH	Reaction	Vapor	4	Kg.-cal./gram mole	−2.7	−6.5	−10.6	−15	−20	−25
ΔF	Reaction	Vapor	5	Kg.-cal./gram mole	−67.6	−76.3	−86.5	−97.4	−108	−115.5
ΔS	Reaction	Vapor	6	E.U./gram mole	130.5	116	110	103	98.5	91
K	Reaction	Vapor	7	Equil. const.	$10^{29.6}$	$10^{27.9}$	$10^{27.5}$	$10^{26.7}$	$10^{26.4}$	$10^{25.5}$
E	Reaction	Vapor	8	Kg.-cal./gram mole	43	45	47	50	52	55
Z	Reaction	Vapor	9	Kg.-cal./gram mole	86	90	94	99	104	109
k	Reaction	Vapor	10	Cc./mole/sec.	0.0001	0.0631	1.6	31.7	317	12,600

Reference Equations

1. $C_p = -16.51 + 0.219T - 0.105 \times 10^{-3}T^2 + \frac{46.5 \times 10^6}{T^3}$

   Based on method of Dobratz (*3*), critical constants by method of Hougen and Watson (*7*)

2. $C_p = 2.36 + 0.131T - 51.04 \times 10^{-6}T^2 + \frac{32.8 \times 10^6}{T^3}$

   Based on same references as Equation 1

3. $C_p = 6.20 + 0.0063T$

   From Hougen and Watson (*8*)

4. $(\Delta H)_T = 5939 - 14.53T - 0.019T^2 - 10^{-6}T^3 + \frac{9.5 \times 10^6}{T^2}$

   From $(\Delta H)_T = \Delta H_{298} + \int_{298}^{T} \Delta C_p dt$ and $\Delta C_p = -14.53 - 0.037T - 3 \times 10^{-6}T^2 - \frac{19.1 \times 10^6}{T^3}$

5. $(\Delta F)_T = (\Delta H)_T - T(\Delta S)_T$

6. $(\Delta S)_T = 232 - 33.5 \log T - 0.037T - 2 \times 10^{-6}T^2$
   From S_T (diphenylamine) $= 303 - 38 \log T + 0.219T - 53 \times 10^{-6}T^2$
   S_T (aniline) $= 26.8 + 5.43 \log T + 0.131T - 25.5 \times 10^{-6}T^2$
   S_T (ammonia) $= 17.5 + 15.41 \log T + 0.0063T$

7. $-(\Delta F)_T = RT\ln K$, R from T_c, P_c

8. $E = Z/2$
   Eyring's method (*6*), assuming a simple bimolecular collision

9. $Z = 83.7$ (energy required to break 1 mole of N—H bonds) $- (\Delta H)_T$

10. $k = Ce^{-E/RT}$
    $C = 10^{15}$ seconds, approximately (*9*)

In subsequent experimentation with the activated aluminas, it was shown that the gel-type, *H* series catalyst, specifically Alcoa *H*-41, was more than twice as active as the *F*-10 variety. For this reason, the *H*-41 was used in the determination of the optimum operating conditions.

In the study of the effect of temperature on conversion, it was found that there was no conversion at any temperature below 360° to 380° C. at space velocities of 0.55 to 2.5 grams of aniline fed per cubic centimeter of catalyst volume. At 380° C. trace conversion was noted, but the amount was too small to be recoverable. Conversion increased rapidly above 400° C. until at 450° C. it varied from 10 to 15% depending on the space velocity used. At 460° C., conversion was considerably higher, varying from 20 to 35% at different space velocities, indicating an increasing effect of temperature. These results are shown in Figure 7, where per cent conversion is plotted against space velocity and against temperature. On running at higher temperatures, it was found that above 470° to 475° C. oxidation and decomposition became increasingly noticeable, until at a temperature around 500° C. the diphenylamine recoverable from the effluent was considerably lower than expected and it was very dark in color. After operation at this temperature, the inside surfaces of the chamber and tubing were coated with a black deposit of carbon and decomposition residue. At 550° C., these effects increased to a point where successful operation was impossible.

In order to determine the effective life of the catalyst under at least one set of conditions, a run was made at the lowest space velocity (*S* = 0.55 gram of aniline fed per cubic centimeter of catalyst volume per hour) and the optimum temperature (460° C.). The results are shown in Figure 8. After 10 hours of continuous operation, production of diphenylamine began to decrease sharply, dropping to less than 30% of its original value within the next 5 hours. At this point, the aniline feed was stopped and air started through the chamber to burn off accumulated impurities, thus, it was hoped, reactivating the catalyst. The reactivation proved to be extremely exothermic, and control of the bed temperatures was at least partially lost. It was later decided from data taken during the run that bed temperatures may have risen to well above 600° or 700° C. This, of course,

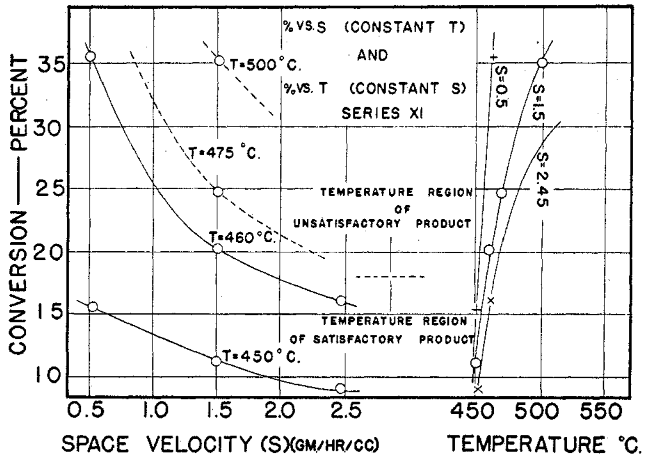


Figure 7. Effect of Space Velocity and Temperature in Single-Pass Diphenylamine Production

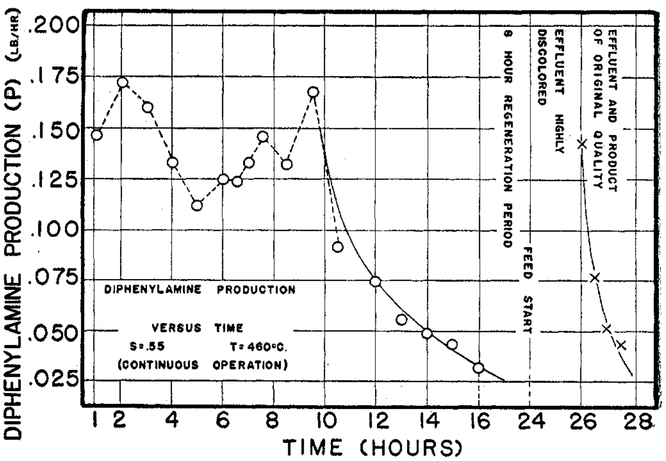


Figure 8. Effect of Time on Rate of Diphenylamine Production

caused permanent damage to the catalyst surface, resulting in the very short life, apparent in Figure 8, during the second reaction cycle. It is to be noted, however, that catalyst activity was at least temporarily restored to its original level upon completion of the reactivation, only the life having been impaired by the excessive temperatures to which it was exposed.

The above constitutes only one set of data, and is, therefore, an insufficient basis from which to draw accurate conclusions, particularly concerning so complex a problem as catalyst regeneration. However, further investigation should very shortly complete the data on this phase of the process, and will be presented in a later paper concerning the kinetics and mechanism of the reaction.

The presence of a slow stream of nitrogen was essential to the successful production of a white grade of diphenylamine. In the absence of nitrogen, a low yield of a very dark product was obtained, indicating considerable oxidation and decomposition had occurred.

RESULTS AND CONCLUSIONS

Activated alumina will catalyze the vapor phase condensation of aniline to diphenylamine, resulting in a rate of reaction which permits the process to be of commercial interest, and producing no side reactions in detectable quantities.

In operation, the process is such that a partial condensation system, involving continuous removal of the diphenylamine as a liquid and recycle of the aniline-nitrogen vapor, should be feasible. This should result in virtually complete reaction of the aniline fed. The diphenylamine produced has a melting point of 51° to 53° C., comparing favorably with the literature value for the pure substance, 52.9° C. Nitrogen carrier gas is used both to sweep the reactant and products along the chamber and also to provide the inert atmosphere necessary to prevent oxidation and decomposition of the materials involved.

Conversion of the aniline to diphenylamine increases with increasing temperature at constant space velocity, first becoming appreciable at temperatures around 400° C. Since decomposition of both aniline and diphenylamine begins at approximately 470° C., this sets an upper limit on the process temperature; 460° C. appears to be the most satisfactory point of operation. Conversion increases with decreasing space velocity, as might be expected.

Based on only one set of data, it seems that the catalyst life is approximately 10 hours. Assuming that regeneration is possible with close control of the process temperature, by limiting either the amount or concentration of air in the regeneration gas mixture, this life should not be too short for industrial purposes. Regeneration of this type of catalyst is accomplished in virtually every other type of installation in which it is used, and there is no apparent reason why regeneration should prove to be impossible in this process. If it is possible, then with several chambers, one in production while the others are on the regeneration cycle, the process should offer many advantages over the present liquid phase batch process, depending upon the scale of production.

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ANTIFOULING PAINTS

Tall Oil and Rosin Derivatives in Toxic Paint Vehicles

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As a result of the huge quantities of rosin consumed in the wartime production of antifouling paints, studies were inaugurated with a view of determining the role of rosin substitutes for use in soluble-matrix antifouling paint. The advent of tall oil in commercial quantities made it an interesting prospect for this study. In addition tall oil esters of glycerol and pentaerythritol were prepared and studied along with abietic acid and hydrogenated methyl abietate as rosin diluents. The esters appear to affect antifouling efficiency and physical durability adversely in direct ratio to the extent to which they are substituted. Abietic acid and hydrogenated methyl abietate improve perceptibly the physical qualities of the film. Tall oil may be substituted for rosin up to 50% without affecting the performance of the paint.

PREVIOUS papers (*1–3*) discussed the effects of various pigment properties on the quality of antifouling paints. The present study reveals information on the properties of matrix constituents as they affect the performance characteristics of the paint. Several theories relating to the mechanism by which successful antifouling coatings function have been proposed. Among the more popular theories is that of Ketchum, Ferry, and Burns (*4*) relating to matrix solubility. These authors have demonstrated that in the design of soluble-matrix paints in which the rate of toxic release is controlled by matrix solubility rosin can play an important role since it possesses an optimum solubility in sea water. Objectionable properties of rosin such as brittleness and poor water resistance require considerable modification before paints of practical durability may be prepared employing rosin as a major matrix ingredient. Since rosin is used extensively as the principal constituent of the matrices of both hot and cold plastic paints, the advent of tall oil in sufficient commercial quantities for such application appeared most interesting as a possible substitute or diluent for rosin in the formulation of soluble-matrix coatings.

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