

Extractive-Distillation Unit for Production of Nitration-Grade Toluene

Chemical Refining of Aromatic Hydrocarbons from Petroleum

TOLUENE TREATING

P. L. BRÁNDT, R. J. LEE, AND F. T. WADSWORTH

Pan American Refining Corporation, Texas City, Tex.

DURING the past several decades it has been common practice to subject crude or raw grades of benzene, toluene, xylene, and various solvent naphthas to sulfuric acid refining in the process of producing "pure" or refined grades of these aromatic hydrocarbons. Such treatment has been used to render the hydrocarbons suitable for nitration purposes and for certain solvent and chemical applications. In the case of aromatic hydrocarbons produced for subsequent nitration, particularly toluene for trinitrotoluene manufacture, the purpose of sulfuric acid treating has been to remove unsaturated hydrocarbons which, if not removed, might lead to the production of an unstable nitrated product or to possible hazards in the nitration operations. There are, however, practically no published data dealing with the basic considerations of toluene treating, aside from a few generalized statements (1, 13, 15) concerning the removal of olefins or unsaturates from toluene by acid treating. It appears that the practice has evolved in the coal tar industry, and, up to the time of World War II, toluene treating has generally been carried out in large batch agitators (15) in what appears to

have been a rather inefficient manner, from the standpoint of acid requirements and toluene losses.

With the advent of World War II and the unprecedented demand for nitration-grade toluene, which was predominantly supplied for the first time by the petroleum industry, many problems were encountered in producing toluene meeting nitration-grade acid-wash color specifications. This was particularly true of toluene synthesized from naphthenes by high temperature dehydrogenation processes—for example, hydroforming—and toluene from high temperature cracking operations. Since practically no information was available on what types of components were responsible for poor acid-wash color, it was difficult to make changes in refining operations to correct deficiencies in this respect. Also, it was not possible to devise other toluene treating methods which would be more satisfactory than sulfuric acid treating. Consequently, investigations were undertaken to determine the types of compounds responsible for poor acid-wash color characteristics, and to devise more effective methods for treating toluene and similar aromatic hydrocarbons.

ACID-WASH COLOR

Of the many specifications for nitration-grade toluene, the acid-wash color specification has been one of the most difficult to meet so far as many petroleum refiners have been concerned. This has been a consequence of the lack of information on the causes of poor acid-wash color and the delayed nature of the problem arising from instability in storage.

The acid-wash color test (4, 7, 21), which was devised by the coal tar industry, was intended to indicate whether the content of undesirable unsaturated hydrocarbons in the toluene was sufficiently low for nitration purposes. This extremely sensitive test comprises shaking the aromatic hydrocarbon (21 ml.) and sulfuric acid (7 ml.) together for 20 seconds at $70^\circ \pm 2^\circ$ F. under specified conditions. After a 15-minute standing followed by slight swirling of the bottle, the color of the sulfuric acid layer (the acid wash) is compared with a set of Barrett color standards (21). In the case of nitration-grade toluene, a minimum acid-wash color of 2 (light amber) was established as representing toluene of satisfactory purity from the standpoint of limiting the content of unsaturated hydrocarbons and possibly other acid-reactive components. However, this empirical test sets no exact limitation on the allowable percentage of unsaturated hydrocarbons, and very little has been known concerning the type or types of components particularly deleterious with respect to acid-wash color. Moreover, no definite specification (such as bromine number) has been set to limit the content of unsaturated hydrocarbons, other than those limitations inherently imposed by the specific gravity specification ($0.871 + 0.032$ at $63/63^\circ$ F.) and the acid-wash color test. These limitations have been more than adequate in the case of toluene refined by treating with sulfuric acid, since practically complete olefin removal was necessary in the acid-treating step in order to meet the acid-wash color specification. However, it has been found that diolefins are chiefly responsible for acid-wash color difficulties, whereas mono-olefins have little effect. Hence, when using the improved treating procedures designed to remove diolefins in particular, as described later, it may be desirable to establish a limiting mono-olefin content to supplement the acid-wash color specification. The exact magnitude of this specification is a matter which should be evaluated in terms of the effect of mono-olefins on nitration of toluene and is beyond the scope of this paper. However, an unnecessarily rigid limitation in this regard should not be imposed, since it would place an undue burden on the refiner and limit toluene supplies in time of emergency.

Other acid-wash color specifications have been established by The Barrett Company and others for various refined grades of benzene, toluene, xylene, and high-solvency naphthas (7, 13). Kenney (13) states in this connection that the acid-wash test is a criterion of the degree of purification that a solvent has received in its manufacture. The impurities removable by acid treating include substances which give rise to gummy bodies on aging, heating, or exposure to air. If present in large amount, the gummy bodies may cause darkening in color. The acid-wash test is, according to Kenney (13), of importance to the paint and varnish industry as a measure of the removal of these impurities to an extent that ensures satisfactory behavior of the solvent.

TABLE I. EFFECT OF AIR AND OXYGEN ON B.O.W. TOLUENE STABILITY TEST

Time on Test, Hr.	A.W.C. on B.O.W. Test		
	With air	With O_2	Heat only
0.0	0-1	0-1	0-1
0.7	...	2+	2-3
2.1	3-4	3-4	3-4
3.1	...	3-4	3-4
4.5	4	3-4	4
8.0	4-5
12.0	5	...	5
16.0	6+

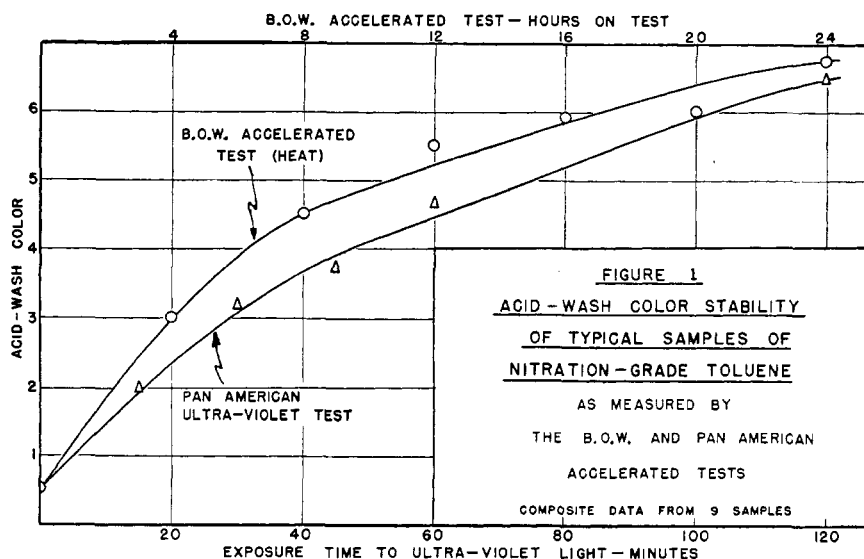
The problems connected with the chemical refining of toluene from petroleum sources were studied, and the application of the information to the refining of various other aromatic hydrocarbons is indicated. Investigations with specific hydrocarbons showed that the presence of diolefins in toluene is harmful in the acid-wash color test, even at low concentrations (0.005-0.01%). Reactions with maleic anhydride confirmed these conclusions. A toluene-treating process using 0.005-0.01% maleic anhydride was shown to produce toluene of exceptional acid-wash color characteristics. Vapor-phase treating with U.O.P. phosphoric acid polymerization catalyst was demonstrated as an effective method of toluene refining. Data are presented on the variables in conventional sulfuric acid treating and on accelerated test methods to compare the efficiency of different treating conditions and to predict the acid-wash color stability of the product.

It is the belief of the authors that the causes of poor acid-wash color and stability, and the improved methods of toluene treating described in this paper, will be widely applicable to various other aromatic hydrocarbons used in the solvent field. Hence, although the present work was confined to nitration-grade toluene, its wider implication should not be overlooked.

ACID-WASH COLOR STABILITY

In addition to the initial acid-wash color of freshly produced toluene, the acid-wash color stability or storage stability of the toluene must be seriously considered in evaluating the merits of different treating processes. Many cases were encountered in the present work, for example, where freshly produced toluene of petroleum origin was found to have satisfactory initial acid-wash color, but its acid-wash color degraded rapidly to an unsatisfactory level in a matter of a few days. To predict the stability of toluene with respect to acid-wash color deterioration, studies were made of storage characteristics *vs.* two accelerated aging tests. One such accelerated test developed by the Humble Oil & Refining Company and the Baytown Ordnance Works (B.O.W.) when properly correlated for toluene from a given source, was found to enable fairly reliable prediction of the actual stability of the toluene during normal storage and shipping periods (at least 1-3 months). Another test, the Pan American rapid ultraviolet test developed in the course of this work, was found to be a valuable test for routine plant control.

The B.O.W. accelerated test developed by the Humble Oil & Refining Company (8) is carried out as follows: Approximately 600 ml. of the sample to be tested are placed in a flask equipped with a reflux condenser and immersed in a water bath maintained at a temperature of $195^\circ \pm 5^\circ$ F. Purified air (sulfuric acid scrubber and caustic tower) is passed through a heating coil also immersed in the heating bath and thence into the sample through a tube of 4-5 mm. inside diameter at a rate such that there is rapid bubbling. Ground-glass joints are used throughout; joint lubricants should be avoided. Samples are taken initially and at 4-hour intervals thereafter for the determination of acid-wash color. The test is run for 24 hours, or until the acid-wash color reaches a value in excess of No. 6 standard. Typical data are shown in Table I. The test results are reported as the acid-wash color after 24 hours—for example, 3-4 A.W.C. after 24 hours—or the time required to reach 6+ color—for example, 6+ A.W.C. in 16 hours. It is important that the test equipment be set up where it will not be exposed to direct sunlight or bright reflected light. Every precaution must also be observed regarding cleanliness in sampling and avoidance of exposure of the samples to sunlight even for a matter of minutes, since sunlight causes extremely rapid degradation of acid-wash color. The importance of this precaution on regular acid-wash color determinations in routine plant sampling operations as well cannot be too strongly stressed.



The effect of bubbling air or oxygen through the sample in the B.O.W. test was found to have little effect on the results obtained, as compared with the accelerating action of heat alone. This is shown for a typical commercial nitration-grade toluene sample in Table I, with the temperature at 200° F. However, the original test procedure using air as described was followed in all work reported here.

Based on extensive experience with toluene produced by hydro-forming followed by extractive distillation (phenol system) and mild sulfuric acid treating (3-5 pounds per barrel), the B.O.W. test results are interpreted qualitatively as follows: excellent and unusual stability if the toluene sample showed an acid-wash color (A.W.C.) of 1-2 after 24 hours on test; good stability for an A.W.C. of 3-6 after 24 hours; satisfactory if A.W.C. is 6 after 12-20 hours; and questionable or unsatisfactory stability if A.W.C. is 6 in less than 12 hours by this accelerated method.

A second accelerated test for acid-wash color stability evaluation—the Pan American ultraviolet test—was developed based upon the accelerating effect of ultraviolet light on acid-wash color deterioration. The advantage of the ultraviolet test over the B.O.W. procedure lies in the fact that a sample can be evaluated in 30-120 minutes as compared to 8-24 hours by the B.O.W. test. For this reason the ultraviolet method is most useful in plant control. However, the B.O.W. test is considerably more sensitive to slight differences in stability and is usually relied upon in connection with tank-car shipments. Because of this greater sensitivity, the B.O.W. method was used as the control test in all investigations reported here regarding improved treating methods and in studies of the factors influencing acid treating and poor acid-wash color.

The Pan American test is carried out in the following manner:

APPARATUS. Mineralite ultraviolet lamp (Model V41, manufactured by Ultra-Violet Products, Inc.) was obtained from the Braun Corporation as No. 361 Mineralight lamp. The equipment consisted of a 250-ml. beaker, a 50-ml. beaker, and a 25-ml. pipet.

PROCEDURE. A sample of 200 ml. at 80-90° F. is placed in a 250-ml. beaker under the center of the window area of the lamp, and the whole apparatus is covered with a cloth or housed in a closed box. The distance from the quartz tube of the lamp to the surface of the toluene is 6-7 cm. Samples (25 ml.) are withdrawn at 20- or 40-minute intervals, and the acid-wash color is determined until it has reached 6+ (usually 2 hours or less). Since the thickness of the toluene layer is gradually decreased by this procedure as the samples are removed, it would appear that the rate of deterioration might vary. It was found in practice, however, that exposing the total 200 ml. sample for 2 hours gave practically the same results as were obtained on the material remaining at the end of 2 hours when 25 ml. samples had been removed at 20-minute intervals.

ALTERNATE PROCEDURE. For plant control purposes the following method was found to be useful as a rapid check on the quality of production: Thirty milliliters of the sample in a 50-ml. beaker are placed directly under the center of the window area of the lamp. The whole apparatus is then covered with a heavy cloth. The sample is exposed for 40 or 60 minutes, and the acid-wash color determined. The results are reported as acid-wash color after 40 or 60 minutes of ultraviolet exposure.

It has been our general experience in plant control work that, if the toluene shows an acid-wash color of 3 or less after 40-minute exposure, the stability will be satisfactory. Unstable and unsatisfactory toluene will show an acid-wash color of 4-6 in 40 minutes or less by this test, although the initial acid-wash color may be completely satisfactory (0-2). A comparison of the results obtained by the B.O.W. and ultraviolet tests is shown in Figure 1. This figure should not be construed to be a general correlation chart between the two methods, since different samples were observed to show some divergence when tested by the two methods. The correlation between the ultraviolet and B.O.W. tests shown in Figure 1 holds fairly well for the first 30-40 minutes of ultraviolet exposure. Thereafter the increase in acid-wash color may be slower on some samples on the ultraviolet test than would be predicted from Figure 1.

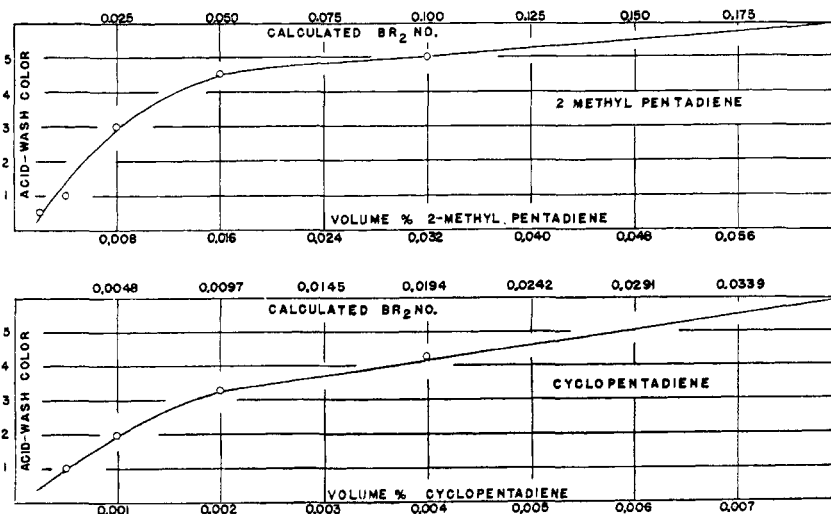


Figure 2. Effect of Diolefins on Acid-Wash Color of Toluene-Diolefin Blends Made Up in Olefin-Free Toluene

TABLE II. EFFECT OF MONO- AND DIOLEFINS ON ACID-WASH COLOR OF TOLUENE

Concn. of Added Compound, %	A.W.C. of Toluene with		
	Mixed C ₈ mono-olefins	2-Methylpentadiene	Cyclopentadiene
0.000	0	0	0
0.005	0-1
0.001	2
0.002	...	0-1	3+
0.003	...	1	...
0.004	...	1	4+
0.006	...	3	...
0.008	...	3	6
0.016	...	4+	...
0.032	...	5	...
0.064	...	6	...
0.167	0
0.67	1
0.79	2+
1.00	3
1.96	4+
3.85	5-6
5.66	6+

COMPONENTS RESPONSIBLE FOR UNSATISFACTORY RESULTS

The cause of unsatisfactory acid-wash color in the case of refined toluene has been attributed in a general way to unsaturated hydrocarbons, principally olefins (15). However, exhaustive studies by Brooks and Humphrey (2) on the refining of cracked distillates showed the importance of removing reactive tar- and resin-forming diolefins for the production of satisfactory motor gasoline. Similar data by numerous other investigators (1, 6, 16, 17) also indicated the deleterious nature of diolefins in gasoline with respect to color (not acid-wash color) and gum formation. By implication, therefore, it was suspected that diolefins might be responsible for unsatisfactory acid-wash color characteristics in the case of toluene. No reports were found in the literature, however, of attempts to determine the effect of the various classes of unsaturates on the acid-wash color of toluene, so that the more deleterious class could be singled out.

The problems of finding the causes of unsatisfactory acid-wash color of toluene was attacked from two standpoints: (a) an investigation to determine the type or types of compounds which would lead to poor acid-wash color and the concentration at which they would be detrimental, and (b) a study involving the treatment of unrefined toluene of poor (6+) acid-wash color with reagents and under conditions known to remove specifically or react with various types of diolefins.

EFFECT OF SELECTED MONO- AND DIOLEFINS. In order to determine the effect of olefins and diolefins on acid-wash color and acid-wash color stability, blends of several individual olefins and diolefins were made with a highly purified sample of toluene. The components of the blends were prepared as follows:

1. Olefin- and diolefin-free toluene: Best quality nitration-grade toluene was further exhaustively treated with 98% sulfuric acid, caustic-washed, and distilled slowly from a flask containing maleic anhydride. The distillate was finally washed with aqueous caustic and water.

2. Isomeric eight-carbon branched-chain mono-olefins (codimer): A sample of codimer produced by the polymerization of mixed butenes was fractionated through a 35-plate laboratory column. The fraction boiling 225-235° F. was separated for this work and treated with 5% maleic anhydride for 2 hours at 200° F. This material possessed a bromine number of 133; this showed it to contain virtually 100% olefins.

3. Aliphatic diolefin (2-methylpentadiene): This compound, purchased from Commercial Solvents Corporation, was a mixture of the difficultly separable 2-methyl-1,3-pentadiene and 2-methyl-2,4-pentadiene. The sample was redistilled prior to use.

4. Cyclic diolefin (cyclopentadiene): This material was freshly prepared from the dimer, dicyclopentadiene (Eastman Kodak Company), by depolymerization over stainless steel turnings at 350° F. followed by fractionation.

In preparing the blends of the diolefins, stock solutions of 1% 2-methylpentadiene and cyclopentadiene, respectively, were made with the toluene (olefin- and diolefin-free) and aliquot portions made up with additional toluene to give the desired concentration. The acid-wash color and accelerated acid-wash color stability were determined on the blends as previously described.

It was soon evident that extremely small quantities of diolefins had a pronounced effect on the acid-wash color. After orientation as to the concentration range required to keep the blends within the range of the acid-wash color standards, a series of blends were prepared to show the effect of concentration of the mono- and diolefins on the acid-wash color. These data are shown in Table II and graphically in Figure 2.

Very low concentrations (0.001-0.01%) of diolefins have a serious effect on the acid-wash color of toluene, whereas C₈ mono-olefins, as represented by codimer, are relatively ineffectual even in concentrations as high as 0.7% corresponding to a bromine number of 1.1. Since diolefins are detrimental in extremely low concentrations, and since mono-olefins appear to have practically no effect on acid-wash color at the concentrations normally encountered, bromine number (or other comparable measure of olefin content) has no significance in predicting acid-wash color or color stability. Furthermore, the more reactive cyclic diolefin (cyclopentadiene) shows a pronounced effect at a considerably lower concentration (0.001-0.002%) than the aliphatic diolefin (2-methylpentadiene). This fact will be referred to again in connection with maleic anhydride treatment of raw toluene.

In hypothetical refining of cyclopentadiene blends from a 6 acid-wash color (0.008% cyclopentadiene) to a 0+ color, a bromine number reduction of only about 0.05 unit is involved; whereas with the aliphatic diolefin the same reduction in acid-wash color would be equivalent to a reduction of 0.2 bromine number. A comparable effect was noticed in the catalytic treating of a sample of commercial toluene. For example, in this catalytic treatment of raw toluene the acid-wash color was reduced from 6+ to 1 while the bromine number reduction amounted to only about 0.05-0.1 unit. This observation is advanced as further confirmatory evidence that reactive diolefins, probably cyclic in nature, are the main cause of unsatisfactory acid-wash color.

ACID-WASH COLOR STABILITY vs. MONO-OLEFIN AND DIOLEFIN CONTENT. The authors' data on the effect of mono- and diolefins on the acid-wash color stability are not so complete as would be desired. However, a number of blends of both types of unsaturates with toluene were prepared and the stability measured by the B.O.W. accelerated test, so that the trend is quite apparent. The data are shown in Table III.

The diolefins also contribute to poor stability of the toluene, whereas mono-olefins seem to have little effect. In the latter case the acid-wash color remains very close to the initial level after accelerated aging. For comparison the data for three typi-

TABLE III. EFFECT OF MONO- AND DIOLEFINS ON ACID-WASH COLOR STABILITY OF TOLUENE

Added Compound	Vol. % Added	A.W.C. of Blend	B.O.W. Accelerated A.W.C. Stability Test					
			4 hr.	8 hr.	12 hr.	16 hr.	20 hr.	24 hr.
None	0.00	0	0+	0+	0+	0-1	0-1	0-1
C ₈ mono-olefins	0.17	0	0-1	0-1	0-1	0-1	3	...
C ₈ mono-olefins	1.00	3	3-4	3-4	3-4	3-4	3-4	6+
2-Methylpentadiene	0.006	2	2	2	2-3	2-3	4-5	6+
2-Methylpentadiene	0.10	6+
2-Methylpentadiene	0.025	3	3+	4	5-6	6+
C ₈ mono-olefins	0.17	3	3+	4	5-6	6+
			A.W.C. Stability					
Typical Tank Car Shipment	Bromine No.	Initial A.W.C.	4 hr.	8 hr.	12 hr.	16 hr.	20 hr.	24 hr.
A	0.07	0-1	4-5	6+
B	0.10	0-1	2-3	3-4	6+
C	0.14	0-1	3-4	5	5-6	6

cal toluene samples from commercial production are included. These were selected to substantiate a previous statement that bromine number is no index of the acid-wash color stability of the sample. Sample A is definitely of questionable stability, although it had the lowest bromine number of the group.

In the light of these data and the fact that toluene produced by hydroforming normally contains only relatively small amounts of diolefins as compared to mono-olefins, which are normally present in concentrations of 1% or less, the most important function of acid treating appears to be the removal of small quantities of diolefins (0.1% or less). It is evident, therefore, that intimate and thorough contacting of sulfuric acid and toluene are necessary for the successful and efficient application of acid treating, especially if small amounts of treating acid (that is, 3 pounds per barrel of toluene) are used.

EFFECT OF MALEIC ANHYDRIDE TREATMENT

From the data just presented on the effects of mono- and diolefins on the acid-wash color of toluene, it appears that conjugated diolefins can be mainly responsible for poor acid-wash color and unsatisfactory acid-wash color stability. Since maleic anhydride is fairly specific for the removal of conjugated diolefins (3, 5), treatment with maleic anhydride should result in a product of improved acid-wash color and improved stability, if conjugated diolefins are present in the toluene and if they are the compounds mainly responsible for bad acid-wash color. Furthermore, the type of diolefin (cyclic or aliphatic) influences the rate and temperature at which reaction with maleic anhydride occurs (1, 3). For this reason a study of the effect of time and temperature in the treatment of raw toluene should give additional information useful in explaining the causes and peculiarities of poor acid-wash color.

MALEIC ANHYDRIDE TREATMENT OF RAW TOLUENE AND TOLUENE OF POOR ACID-WASH COLOR STABILITY. A sample of plant acid-treated toluene of poor stability was treated with 0.28 weight % of maleic anhydride for 2 hours at 200° F. Unreacted maleic anhydride and reaction products were removed by washing with 15% potassium hydroxide, and the treated toluene was distilled. A control sample was given identical treatment except that no maleic anhydride was used. Table IV shows the surprisingly good stability of the toluene treated with maleic anhydride as compared with the poor stability of the control sample.

TABLE IV. MALEIC ANHYDRIDE TREATMENT OF TOLUENE AT 200° F. FOR 2 HOURS

Sample Treated	Maleic Anhydride Used, %	B.O.W. Accelerated A.W.C. Stability Test					
		Initial	4 hr.	8 hr.	12 hr.	16 hr.	20 hr.
Acid-treated toluene	None	0+	3-4	6+
Same, M.A.-treated	0.28	0+	0+	0+	0+	0+	1
Raw toluene	None	6+	2	3-4	4-5	5-6	...
Same, M.A.-treated	0.20	2	2	3-4	4-5	5-6	...
Same, M.A.-treated	1.0	1	1-2	1-2	1-2	2+	3+
Typical tank car shipment of satisfactory toluene	None	0-1	2-3	4-5	5-6	6+	...

In view of the effectiveness of maleic anhydride treatment in stabilizing acid-treated toluene, some work on the treatment of raw toluene (not previously acid-treated) seemed in order. Samples of raw toluene of 6+ acid-wash color were treated in one case with 1% and in another example with 0.2% of maleic anhydride for 2 hours at 200° F. Caustic washing followed; no distillation step was used. Other data in Table IV show that treatment with maleic anhydride alone produced a color-stable toluene without sulfuric acid treatment; this is convincing evidence that con-

jugated diolefins are responsible for the unsatisfactory acid-wash color and color instability of incompletely refined toluene.

The evidence of the presence of a reactive conjugated diolefin in raw toluene was just presented. If this type of diolefin is present, maleic anhydride treatment at room temperature (80-90° F.) rather than at 200° F. should be effective in reducing the acid-wash color and stabilizing the toluene. This proved to be the case. For example, raw toluene of 6+ A.W.C. was treated with 1% maleic anhydride for 20 minutes at 80° F. The treated toluene was caustic-washed and filtered; acid-wash color and color stability were then determined. The acid-wash color after treatment was 2-3, and a 3+ A.W.C. was obtained after 24 hours on the B.O.W. accelerated stability test. Removal of the reactive diolefins is seen to improve the initial acid-wash color from 6+ to 2-3. Of even greater interest is the fact that the unsaturates, some of which are probably relatively unreactive diolefins, remaining after this maleic anhydride treatment do not contribute appreciably to poor acid-wash color stability. It seems then that if the most reactive diolefins are removed from the raw toluene, even though the acid-wash color is not reduced to 0-1, the toluene is extremely stable against further deterioration. This fact is confirmed in the work on treatment of raw toluene with phosphoric acid polymerization catalyst described later.

RESTORATION OF ACID-WASH COLOR OF FINISHED TOLUENE DETERIORATED TO 6+ A.W.C. The mechanism of the reaction which accounts for the deterioration of acid-wash color is obscure. The nature of the degradation products formed by this reaction are also unknown. To clarify this situation at least partially, a sample of refined toluene (initial A.W.C. = 0+) was deteriorated to 6+ A.W.C. by means of the B.O.W. accelerated test by heating at 200° F for 16 hours. The resultant toluene sample, now of 6+ A.W.C., was given the following successive maleic anhydride treatments:

Maleic Anhydride, %	Time of Reaction, Hr.	Temp., ° F.	A.W.C. after Treatment Shown
None	6+
1	0.4	200	4+
3	2.0	200	3+
3	5.0	200	3

It would appear that the degradation products causing the deterioration in acid-wash color are not entirely compounds reactive with maleic anhydride, since even the comparatively drastic succession of maleic anhydride treatments described did not reduce that color to the original value (0+). Moreover, the compounds present in unrefined toluene which are responsible for the high A.W.C. are not the same as the compounds present in refined toluene which has deteriorated in acid-wash color; the former can be practically completely removed with maleic anhydride treatment, whereas the latter cannot. This suggests that A.W.C. deterioration is caused, at least in part, by the polymerization of conjugated diolefins to higher polymers of non-conjugated structure.

EFFECT OF TREATMENT TIME WITH MALEIC ANHYDRIDE. It was shown in the preceding discussion that the acid-wash color of unrefined toluene could be reduced from 6+ to 1 by means of treatment solely with 1% maleic anhydride. The stability of the toluene so treated was found to be much superior to that of toluene generally produced by commercial acid treating.

The effect of time of maleic anhydride treatment on the reduction in acid-wash color of raw toluene (6+ initial A.W.C.) was studied next. A sample of raw toluene was heated to 200° F. at which time 1% by weight of maleic anhydride was added and vigorously agitated; 25-ml. samples were withdrawn at regular time intervals and immediately shaken with 15% potassium hydroxide to quench the reaction. The toluene layer was separated and filtered to remove suspended water; after that the acid-wash color was determined. The treated toluene was not distilled, since distillation was shown to be unnecessary with maleic anhydride treatment. The data, shown in the following

table, were obtained for raw toluene (bromine number 0.31) treated with 1% by weight of maleic anhydride at 200° F.:

Time of Treating, Min.	Acid-Wash Color	Time of Treating, Min.	Acid-Wash Color
0	6+	7	2
1	3+	10	2
2	3+	20	2
3	3	120	1
5	3		

The initial rate of removal of the undesirable diolefins is rapid since the acid-wash color decreased from 6+ to 3+ during 1 minute of treatment, whereas 20 minutes were required for a further decrease to 2 A.W.C. and 100 additional minutes for 1 A.W.C. From the rate of reaction observed, there is evidence of the presence of two or more types of conjugated diolefins—that is, a very reactive diolefin, probably cyclic, which reacts with maleic anhydride almost instantaneously, and a less reactive type which reacts only very slowly. Similar conclusions were reached by Birch and Scott (1) in studies concerned with the identification of the diolefins in the low-boiling fractions of vapor phase cracked gasoline. It is also of possible interest that Kramer and Spilker (14) isolated the reactive cyclopentadiene from coke-oven benzene.

STABILIZATION OF ACID-TREATED TOLUENE WITH MALEIC ANHYDRIDE

Experience has shown the toluene, which has been refined by sulfuric acid treatment and which meets all specifications for nitration grade toluene, frequently deteriorates on storage to a point where the A.W.C. is greater than the specification limit of 2. When this occurs, it invariably entails reprocessing of the toluene together with any other contaminated production. Since preliminary experiments showed the remarkable stabilizing effect of maleic anhydride treatment against acid-wash color deterioration, and since only small quantities (0.01% or less) of maleic anhydride were required, it appeared that this method of treating could be advantageously employed on a commercial scale. Accordingly, further development of this procedure was carried out particularly with reference to optimum maleic anhydride concentration, temperature, and time of treatment.

Data from the maleic anhydride treatment of four toluene samples of widely divergent character previously refined by sulfuric acid treatment are collected in Table V. The A.W.C. stability data for samples A and B indicate that maleic anhydride treatment effectively stabilizes freshly produced toluene against A.W.C. deterioration; moreover, the quantities of maleic anhydride required are extremely small, of the order of 0.005–0.01%.

Samples C and D, representing finished toluene which had deteriorated in storage to high A.W.C. (5 and 6+), exemplify

the ability of maleic anhydride partially to reduce the initial A.W.C. and to stabilize the A.W.C. at the reduced value. Generally speaking, a reduction in A.W.C. of 1–1.5 units can be expected when toluene of 2–5 A.W.C. is treated with 0.01% maleic anhydride. The important point, however, is that the acid-wash color is stabilized at this reduced level.

Maleic anhydride is not an inhibitor in the sense of a gasoline inhibitor which is added permanently to the gasoline. The mechanics of maleic anhydride treating comprise dissolving maleic anhydride in the toluene for a short period and then removing the unreacted maleic anhydride and adduct (reaction product) by caustic washing. The maleic anhydride thereby reacts with the undesirable reactive diolefins which are responsible for A.W.C. difficulties forming a stable acidic reaction product which is removed from the toluene by caustic washing.

A patent issued to I. G. Farbenindustrie (9) claims the use of maleic anhydride for purification of crude benzene from coke ovens or gas plants. The treatment as described recommends adding 0.3–10% (preferably 1–3%) of maleic anhydride to crude benzene, refluxing for 2 hours, and distilling off the purified benzene. In the case of the stabilization of acid-treated toluene as described in this report, only trace amounts (0.005–0.01%) of maleic anhydride and short reaction times at 90–100° F. are required, whereas the 1–3% figures are economically unattractive. This work is further described in a patent recently issued to one of the authors (20).

CATALYTIC TREATING OF TOLUENE

The previous section established quite definitely that diolefins are the main cause of acid-wash color problems associated with nitration-grade toluene production; consequently, certain catalysts known to effect the polymerization of diolefins should be effective for the treatment of toluene. A few preliminary experiments showed that unrefined toluene can be treated with either Attapulgus clay or solid phosphoric acid polymerization catalyst (7, 12) to give an improvement in the acid-wash color. Both liquid-phase and vapor-phase treating were tried with results shown in Table VI.

TABLE VI. PRELIMINARY EXPERIMENTS IN ONE-HOUR CATALYTIC TREATING OF RAW TOLUENE OF BROMINE NO. 0.31

Catalyst	Wt. % Catalyst	Method of Treating	Temp., ° F.	A.W.C.	Catalyst Life Reached, Bbl./Ton
.....	..	No treatment	...	6+	...
Attapulgus clay	16.4	Liquid phase	230	5–6	40
	16.4	Liquid phase	450	4–5	40
	..	Vapor phase	230	6+	15
Phosphoric acid polymerization catalyst ^a	3.3	Liquid phase	230	4	200
	3.3	Liquid phase	450	3	200
	..	Vapor phase	230	1+	50

^a Catalyst used had reached maximum economical life in commercial propylene-butylene polymerization.

TABLE V. STABILIZATION OF H₂SO₄-TREATED TOLUENE BY MALEIC ANHYDRIDE TREATMENT AT 89° F.^a

Sample Designation	Treatment		A.W.C. after Treatment	B.O.W. Accelerated A.W.C. Stability Test					
	Maleic anhydride, %	Time, min.		4 hr.	8 hr.	12 hr.	16 hr.	20 hr.	24 hr.
A	0	0	0–1	2–3	3+	5+	5–6	6	6+
	0.01	5	0–1	0–1	0–1	0–1	0–1	0–1	0–1
B	0	0	0–1	4	4–5	4–5	4–5	4–5	5
	0.01	0.5	0–1	1	1–2	...	2	...	3–4
	0.01	1.0	0–1	1	1–2	...	2	...	2–3
	0.01	2.5	0–1	1	1–2	...	1–2	2	2–3
	0.005	2.5	0–1	1+	1–2	2	2	2	3+
C	0	0	5	6+
	0.01	30	3–4	3–4	3–4	3–4	3–4	4–5	4–5
D	0	0	6+ ^b
	0.01	30	6+
	0.1	30	6+
	1.0	30	4–5	5+	5–6	5–6	5	5	5+

^a Samples A and B were taken at different times from plant production; samples C and D were toluene samples which had deteriorated in plant storage. All four samples had been refined originally by conventional sulfuric acid treating and met all nitration-grade toluene specifications.

^b Estimated to be 7–8 A.W.C.

The liquid-phase treatments at 230° F. were conducted by refluxing the toluene with the catalyst at atmospheric pressure. The experiments at 450° F. were conducted in a steel bomb of the rocking type. The vapor-phase studies were made at atmospheric pressure in a glass reactor. In all cases the treated product was redistilled to remove polymers before determining acid-wash color. The preliminary results indicated that the vapor-phase treating of raw toluene with U.O.P. solid phosphoric acid polymerization catalyst (10) was most promising. This method of treating is similar to that described by Ipatieff and Corson (12) for the vapor-phase refining of cracked gasoline to improve color (Saybolt) and reduce gum-forming tendencies.

PARTIAL LIFE TEST ON U.O.P. POLYMERIZATION CATALYST. The catalyst used in this continuous partial life study was standard U.O.P. solid phosphoric acid catalyst composed of

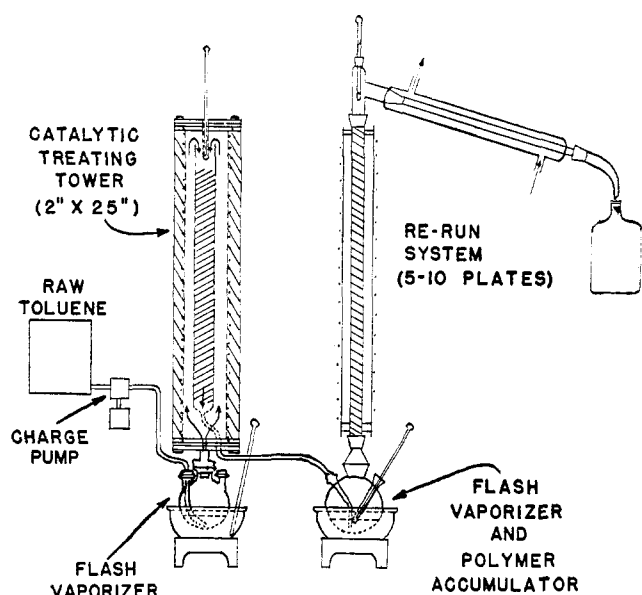


Figure 3. Catalytic Treating Equipment

phosphoric acid on kieselguhr (5, 12). The catalyst had previously been used in the Pan American commercial polymerization unit on the polymerization of propylene and butylenes (11) until the catalyst was considered economically unsuitable for further use. This spent catalyst was employed, since there was a large supply available for potential toluene treating purposes; hence catalyst costs would be negligible if commercial application were undertaken.

The treating studies were conducted in a continuous manner up to a catalyst life of 1130 barrels of toluene per ton of catalyst (178 pounds per pound). The apparatus is shown in Figure 3, which is self-explanatory. The polymer produced in the treating operation accumulated in the rerun-tower pot. The results from this work are summarized in Table VII. These data show that the initial A.W.C. and the A.W.C. stability measured by the B.O.W. and ultraviolet accelerated procedures were good throughout the test. This is an alternative toluene treating procedure which appears quite attractive.

Treatment with U.O.P. polymerization catalyst lowers the bromine number only slightly (0.31 to 0.22), whereas normal plant and laboratory acid treatments (5 pounds of 98% sulfuric acid per barrel) usually reduce the bromine number to 0.05–0.1; yet both methods of treating give a product of satisfactory acid-wash color. The explanation for this surprising difference has been outlined in the previous sections where it was shown that mono-olefins have little or no effect on acid-wash color, whereas diolefins cause serious color difficulties. Apparently this vapor-phase treating method removes predominantly only the more reactive and undesirable diolefins.

SULFURIC ACID TREATING OF TOLUENE

Comprehensive studies were carried out on the refining of toluene with sulfuric acid. The crude toluene used was produced commercially by hydroforming (catalytic dehydrogenation) of petroleum naphthas rich in methylcyclohexane followed by extractive distillation using phenol as solvent. Space limitations make it impossible to present all the data obtained; however, some of the more pertinent data are presented in the following sections.

No data were found in the literature dealing with the variables in sulfuric acid treating of toluene. There are, however, several excellent references (2, 6, 16, 17, 19) on the acid treating of cracked gasolines and the like, since acid refining dates back to the nineteenth century (18).

The preceding work showed that the problem of toluene treating to give a product of good A.W.C. and A.W.C. stability actually resolves itself into the removal of very small quantities (0.1% or less) of diolefins. The mono-olefins which are present to a greater extent, although less detrimental, will also be removed simultaneously with the diolefins. It is evident, therefore, that intimate contacting of the sulfuric acid and toluene is necessary for successful application of acid treating. Moreover, because of the interrelation of the many treating variables, a thorough knowledge is required of the effect of contact time, temperature, and quantity and concentration of acid on treating efficiency.

COMPARISON OF TREATING EFFICIENCY OF 98, 93, AND 87% SULFURIC ACID. There is no doubt that 98% sulfuric acid is the most effective of these three acids; however, the higher the acid concentration, the greater the acidity of the acid-treated toluene; hence the problem of caustic washing becomes more difficult. In addition, the losses of toluene through sulfonation are much larger in treatment with 98% acid. For these reasons a comparative study of the efficiency of 98, 93, and 87% sulfuric acid was made. Figure 4 shows the reductions in unsaturate content (as measured by the bromine number) attainable by the acid treating of raw toluene using various amounts of 98, 93, and 87% sulfuric acid. In the work reported, the quantity of acid employed is expressed as pounds of 98% acid (or equivalent) per barrel (42 gallons or 305 pounds) of toluene. For orientation purposes, therefore, a 3 pound per barrel treat is virtually equivalent to treating with 1 weight % of sulfuric acid. It is noteworthy that 14.5 and 4.5 pounds of H_2SO_4 per barrel of toluene were required when used in 87 and 93% concentration to give the same reduction in unsaturate content as a 3 pound per barrel treatment with acid of 98% concentration (Figure 4). For this reason the use of 87% acid is not to be recommended in commercial treating operations. Further comparisons based on acid-wash color stability data of the treated and redistilled toluene are as follows.

Samples of raw toluene (bromine number 0.67) were treated in glass bottles (approximately two thirds full) for 15 minutes in a Schaerr mechanical shaking machine, in a series of treatments with various quantities of 98, 93, and 87% sulfuric acid. Intimate contacting was obtained in this mechanical shaker, which oscillated horizontally at approximately 425 strokes per minute. After 30 minutes of settling time, samples were taken for determination of acidity; after caustic washing, another set of samples was taken for bromine number determinations. This method was also used in the work which follows.

TIME OF CONTACT vs. ACID REQUIREMENTS. A comparison of 98 and 93% sulfuric acid and spent alkylation acid was also made in which the A.W.C. stability of the treated toluene was used as a criterion of the relative treating efficiencies. Data were obtained simultaneously concerning the effect of time of contact on A.W.C. stability when these three acids were used. Mixing of acid and toluene was achieved in a mechanical shaker as discussed previously. This comparative study (Table VIII) showed that, when treating with fresh 98% sulfuric acid, 1–2 minutes of laboratory contacting resulted in a finished toluene of

TABLE VII. TREATING OF RAW TOLUENE WITH SPENT U.O.P. POLYMERIZATION CATALYST

(Charge, raw toluene, bromine No. 0.31, 6+ A.W.C.; temperature, 230° F.; pressure, atmospheric; rate, 5.7 barrels per ton per hour or 0.7 volume per volume per hour)

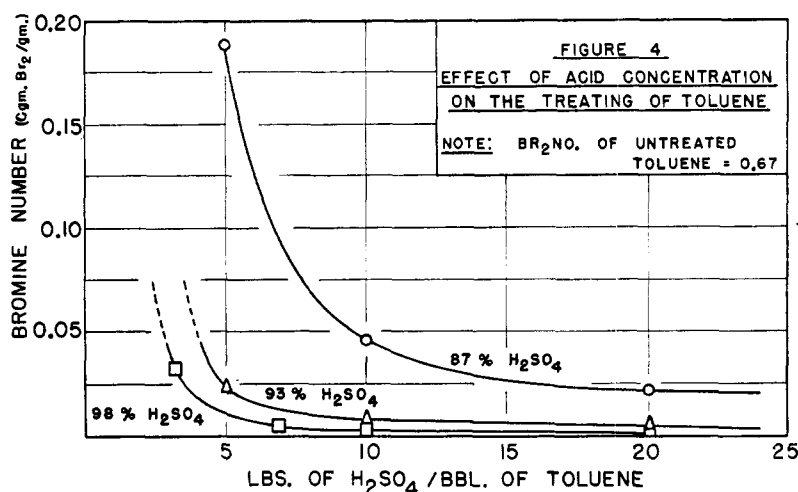
Catalyst Age, Bbl./Ton	A.W.C. of Rerun Overhead		
	As produced	After 40-min. ultraviolet test	After 24-hr. B.O.W. test
23	0-1	1+	1-2
68	1	2	1
433	1+	2+	...
684	1-2	3+	3-4
913	1+	2-3	...
981	2	2-3	...
1028	1-2	3	...

excellent A.W.C. stability, whereas, with 93% acid and particularly with discarded alkylation unit acid, substantially longer contact times (5-20 minutes) were required to yield toluene of similar stability.

Table IX shows that the average effective contact time in the continuous-type commercial acid treating plant of this corporation (orifice mixers and time drum) is equivalent to about 0.5-1.0 minute of laboratory treating. Therefore, spent alkylation acid and 93% sulfuric acid are not to be recommended for use in many commercial toluene treating plants of similar design: In order to produce toluene of good stability by treatment with these less concentrated acids, laboratory contact times of 5-10 minutes were necessary. These longer contact times, based on equivalence to laboratory mixing, are probably not obtainable in most continuous commercial units. With batch treating methods, where long contact periods would be available, any of the acids mentioned would be satisfactory and in many cases more economical.

The laboratory contact times referred to here represent actual minutes of intimate and persistent dispersal of acid in toluene. Accordingly, residence time in a plant acid mixer of inefficient design should not be confused or construed to be equivalent to these laboratory contact times. Rather, the A.W.C. stability data on toluene samples representative of plant operations should be compared with the corresponding A.W.C. in Tables VIII and IX or similar tabulations; the equivalent laboratory contact time can then be obtained as the value corresponding to the point of matching of laboratory and plant A.W.C. stability data obtained by the B.O.W. accelerated test. This comparison is helpful in correlating plant and laboratory studies, and provides a means of checking the efficacy of changes in mixer design or other variables.

The quantity of acid (pounds per barrel) required for treating toluene to a definite A.W.C. stability varies with the available acid contact time, and, conversely, the minimum contact time can be lowered by increasing the quantity of acid used. This relation was studied for common ratios of acid to toluene (3, 5, and 10 pounds of 98% acid per barrel) over a fairly wide range of contact times (Table IX). These data show that the A.W.C. stability of the treated toluene at constant contact time can be markedly improved by increasing the quantity of acid from 3 to 5 to 10 pounds per barrel. The disadvantage to this expedient of using



larger quantities of acid to counteract poor mixing lies in the fact that toluene losses through sulfonation are increased, and obviously acid and possibly caustic costs are greater.

In connection with this work on the effect of contact time in acid treating, data were also accumulated showing the increase in the acidity of acid-treated toluene and decrease in bromine number as a function of contact time (Table X). These data, particularly in graphical form, show that the acidity developed in toluene treating increases rapidly during the first 5 minutes of contacting, and thereafter the rate of change is slight; this shows that the sulfonating ability of the acid has been expended. Therefore since toluene of good A.W.C. stability can be produced by acid treating for an equivalent (to laboratory) contact time of 1-2 minutes, as shown in the preceding section, it would not be desirable to use longer contact times, because not only would greater toluene losses ensue through sulfonation, but a heavier load would be thrown on the caustic treating system.

TREATING TEMPERATURE. The effect of increasing the temperature of treating from 90° to 130° F. was studied at acid contact times ranging from 0.5 to 2.0 minutes; the data are presented in Table XI.

TABLE VIII. TIME OF CONTACT *vs.* ACID-WASH COLOR STABILITY, AND COMPARISON OF 93 AND 98% H₂SO₄ WITH SPENT ALKYLATION ACID IN ACID TREATING OF TOLUENE

(Raw toluene treated, bromine No. 0.30; temperature of treating, 90° F.; settling time, 30 minutes; further treatment, toluene phase caustic-washed and redistilled)

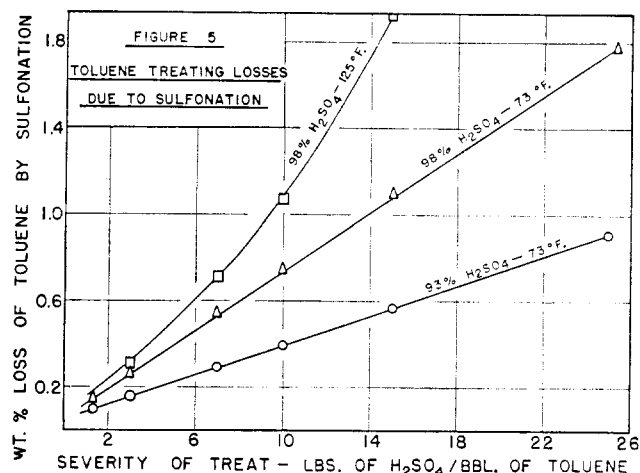
Time of Contact ^a , Min.	B.O.W. Accelerated A.W.C. Stability Test on Treated Toluene						
	Initial	4 hr.	8 hr.	12 hr.	16 hr.	20 hr.	24 hr.
5 Lb. Spent Alkylation Acid/Barrel Toluene							
3	1	1	3-4	5+	6+
7	0-1	0-1	1-2	1-2	3-4	4-5	4-5
10	1	1	1-2	2-3	3	3+	3+
20	0-1	0-1	0-1	0-1	0-1	0-1	0-1
5 Lb. Fresh 93% H ₂ SO ₄ /Barrel Toluene							
0.5	2-3	4-5	6+
1	2	1-2	2	5	6+
2	1-2	1-2	3-4	3-4	4	5-6	...
5	0-1	0+	0-1	0-1	1-2	1-2	1-2
15	0+	0+	0+	0+	0+	1	0-1
5 Lb. Fresh 98% H ₂ SO ₄ /Barrel Toluene							
0.5	0-1	3-4	5-6	6+
1.0	1	2	3-4	5	5-6	6	6+
2.0	0-1	0-1	0-1	0+	0-1	1	1-2
5.0	0+	0+	0-1	1	1	1+	1-2
15.0	0+	0+	0+	0+	0-1	0-1	0-1

^a Treatment in mechanical shaker.

TABLE IX. TIME OF CONTACT AND QUANTITY OF 98% H₂SO₄ *vs.* ACID-WASH COLOR STABILITY IN ACID TREATING OF TOLUENE (Raw toluene treated, bromine No. 0.30; settling time, 30 minutes; further treating, toluene phase caustic-washed and redistilled)

Time of Contact ^a , Min.	B.O.W. Accelerated A.W.C. Stability Test after Heating Time of						
	Initial	4 hr.	8 hr.	12 hr.	16 hr.	20 hr.	14 hr.
3 Lb. 98% H ₂ SO ₄ /Barrel Toluene at 90° F.							
2	1	3-4	5-6	5-6	6+
3.5	0-1	1	2	3-4	4	4	4-5
5	0-1	0-1	1	2-3	3-4	3-4	4+
8	0+	0-1	0-1	0-1	1	1	1
12	0+	1	0-1	1	1	2-3	2-3
5 Lb. 98% H ₂ SO ₄ /Barrel Toluene at 90° F.							
0.5	0-1	3-4	5-6	6+
1	1	2	3-4	5	5-6	6	6+
2	0-1	0-1	0-1	0+	0-1	1	1-2
5	0+	0+	0-1	1	1	1+	1-2
15	0+	0+	0+	0+	0-1	0-1	0-1
10 Lb. 98% H ₂ SO ₄ /Barrel Toluene at 90° F.							
0.25	1-2	3-4	6+
0.50	0+	0+	1-2	1-2	1-2	3-4	4-5
Typical Plant Acid Treating, 3 Lb. 98% H ₂ SO ₄ /Barrel Toluene at 90-95° F.							
Unknown ^a	0-1	3-4	5	6+
Typical Plant Acid Treating, 5 Lb. 98% H ₂ SO ₄ /Barrel Toluene at 120° F.							
Unknown ^a	0-1	3-4	4-5	5-6	6+
	0-1	1-2	3-4	4-5	5	5-6	6+

^a Comparison of the B.O.W. stability of the product with the data from laboratory treats indicates the contact time in the plant to be equivalent to 0.5-1.0 minute of controlled laboratory treating.



The enhanced A.W.C. stability resulting from acid treating at the higher temperature (130° F.) is evident. The disadvantages to this method of increasing treating efficiency are increased equipment corrosion and substantially greater toluene losses due to increased sulfonation at the higher temperature. These objections are not too serious, however, especially if the use of high temperatures constitutes the difference between toluene production of satisfactory A.W.C. stability and unstable production.

TOLUENE LOSSES IN ACID TREATING SYSTEM. Losses of toluene in the acid treating system occur in three ways: (a) Toluene is sulfonated by the sulfuric acid and converted to toluene sulfonic acids, part of which dissolve in the acid sludge, and the remainder, dissolved in the toluene phase, are removed in the caustic washing step; (b) toluene is alkylated by the unsaturates present in raw toluene, the resulting alkylated toluenes being removed as bottoms in the final rerun tower; and (c) toluene is lost by entrainment in the acid sludge and with the spent caustic. With adequate settling time, the latter loss should be small.

The loss of toluene through sulfonation, which comprises the major part of the total loss, was accurately evaluated by laboratory work on olefin-free toluene during treatment with various

quantities of 98% acid at both 73° and 125° F.; the sulfonation loss encountered in treatment with 93% acid at 73° F. was also determined. These loss data were deduced from laboratory treats using accurately weighed quantities of acid and toluene, measuring weights and volumes of the two phases after treating, determining the acidity of the hydrocarbon phase, and assuming the only reaction involved was sulfonation of toluene; this is a reasonable premise under the conditions employed. These data (Figure 5) indicate that sulfonation losses are practically twice as great for treatment with 98% as for treatment with 93% acid, irrespective of the quantity of acid used. Losses are also seen to increase with an increase in treating temperature. Under average treating conditions (3-7 pounds acid per barrel), a loss of 5 barrels per 1000 barrels treated can be expected.

CONCLUSION

The problem of refining toluene from petroleum sources to a product of satisfactory acid-wash color and acid-wash color stability is shown to be intimately connected with the presence of certain reactive olefins. Investigations with pure hydrocarbons showed that diolefins are harmful in the acid-wash color test even at very low concentrations (0.005-0.01%). Most mono-olefins have little effect on acid-wash color. Reactions with maleic anhydride confirmed these conclusions, and it is shown possible to refine toluene recovered from hydroformed naphthas with maleic anhydride.

Vapor-phase treating with U.O.P. phosphoric acid catalyst is shown to be an effective method of toluene treating. Data are also presented on the variables in conventional sulfuric acid treating.

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This paper summarizes experimental work carried out at the Pan American Refining Corporation during World War II in connection with the refining of nitration-grade toluene produced by hydroforming petroleum naphthas. The data have been previously supplied to the United States Army Ordnance Department and the Toluene Technical Committee in the form of reports. The present paper consolidates and summarizes the more pertinent points of general interest and of possible wider application in the field of chemical refining of aromatic hydrocarbons.

LITERATURE CITED

- (1) Birch and Scott, *IND. ENG. CHEM.*, **24**, 29 (1932).
- (2) Brooks and Humphrey, *J. Am. Chem. Soc.*, **40**, 822-56 (1918).
- (3) Diels and Alder, *Ann.*, **460**, 98 (1928); **470**, 62 (1939); *Ber.*, **62**, 554 (1929).
- (4) Down, *J. Soc. Chem. Ind.*, **51**, 28-34, 45-9 (1932).
- (5) Farmer and Warren, *J. Chem. Soc.*, **1929**, 897.
- (6) Halloran, "Science of Petroleum," p. 1798, London, Oxford University Press, 1938.
- (7) Hoffert and Claxon, "Motor Benzol," pp. 769 and 774, London, Natl. Benzol Assoc., 1938.
- (8) Humble Oil & Refining Co., private communications.
- (9) I. G. Farbenindustrie A.-G., Brit. Patent 352,164 (1930).
- (10) Ipatieff, U. S. Patents 1,993,513, 2,018,065, 2,018,066, 2,020,649 (1935); Ipatieff and Schaad, *Ibid.*, **2**, 120,702 (1938); **2**, 157,208 (1939); **2**, 275,182 (1942).
- (11) Ipatieff and Corson, *IND. ENG. CHEM.*, **27**, 1067 (1935); **28**, 860 (1936).
- (12) *Ibid.*, **30**, 1316 (1938).
- (13) Kenney, J. A., in Mattiello's "Protective and Decorative Coatings," Vol. I, pp. 628 and 638, New York, John Wiley & Sons Inc., 1941.
- (14) Kramer and Spilker, *Ber.*, **29**, 553 (1896).
- (15) McBride, Reinicker, and Dunkley, "Toluol Recovery," Booklet 117, U. S. Bureau of Standards, Dec. 19, 1918.
- (16) Morrell, *IND. ENG. CHEM.*, **19**, 794 (1927).
- (17) Sager, *J. Inst. Petroleum Tech.*, **20**, 138 (1934); **22**, 609 (1936).
- (18) Silliman, *Am. Chemist*, **2**, 18 (1871).
- (19) Stratford, Graves, and Brown, *Refiner Natural Gasoline Mfr.*, **17**, 109 (1938).
- (20) Wadsworth, U. S. Patent 2,380,561 (1945).
- (21) Weiss, *IND. ENG. CHEM.*, **10**, 1006 (1918).

TABLE X. EFFECT OF CONTACT TIME ON ACIDITY AND BROMINE NUMBER IN SULFURIC ACID TREATING OF TOLUENE AT 80° F.

Time of Acid Contacting, Min.	Treatment with 3 Lb. 98% H ₂ SO ₄ /Bbl.		Treatment with 10 Lb. 98% H ₂ SO ₄ /Bbl.	
	Acidity ^a	Bromine No. ^b	Acidity ^a	Bromine No. ^b
Charge	0.0	0.33	0.0	0.50
1	0.32	0.26	0.18	0.08
2	0.33	0.26	0.20	0.07
3	0.35	0.13
4	0.37	0.11
5	0.37	0.06	0.48	0.02
10	0.37	0.01	0.53	0.02
20	0.37	0.01	0.63	..
30	0.73	0.01

^a Acidity expressed as weight per cent toluene sulfonic acid.

^b Bromine number expressed as centigrams of bromine absorbed per gram of sample (modified Francis method).

TABLE XI. EFFECT OF TEMPERATURE OF ACID TREATING ON A.W.C. STABILITY

(Raw toluene treated, bromine No. 0.30; quantity of acid; 5 pounds of 98% H₂SO₄ per barrel of toluene)

Contact Time, Min.	Temp. of Treating, ° F.	A.W.C. ^a After Heating Time of						
		Initial	4 hr.	8 hr.	12 hr.	16 hr.	20 hr.	24 hr.
0.5	90	0-1	3-4	5-6	6+
0.5	130	0-1	1	4+	5+	6+
1.0	90	1	2	3-4	5	5-6	6+	6+
1.0	130	0-1	0-1	0-1	0-1	0-1	1	1
2.0	90	0-1	0-1	0-1	0+	0-1	1	1-2

^a B.O.W. accelerated stability test.