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QUANTITATIVE CHEMICAL DETERMINATION OF HYDROCARBONS
IN LACQUER THINNERS

BY
H. E. ASHTON

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Quantitative Chemical Determination Of Hydrocarbons In Lacquer Thinners

By H. E. ASHTON
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¹This paper describes investigation of the chemical method for the determination of the amount of hydrocarbon in lacquer thinners. As hydrocarbons are relatively inexpensive an accurate method is required for controlling their content in lacquer thinners. The chemical method was developed because many paint laboratories do not have the complex instruments necessary for physical measurement of solvent composition.

Two component mixtures were treated first to see if a relationship existed between the treatment and the volume recovered. Mixtures of a hydrocarbon, usually toluene, and an active or latent solvent for nitrocellulose were extracted with different combinations of water, diluted acid, and concentrated sulfuric and phosphoric acids. Water-miscible extractants and a modified Babcock procedure were also tested. The volume of isolated hydrocarbon was measured and its purity determined by refractive index after initial work had shown that this method was accurate. Preliminary washes with water and diluted acid proved beneficial before extraction with concentrated acid.

The better procedures were applied to four different types of lacquer thinners. With three thinners which were of the usual type, the extraction procedures were improvements over the original method. Three procedures gave volume recoveries of over 97%. The method using the Babcock bottle was the only suitable one for a thinner of the "high-low" type but was unsatisfactory for the conventional thinners.

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INTRODUCTION

In recent years many of the newly introduced analytical techniques have involved physical measurements using complex instruments. Such methods include gas phase chromatography, infra-red spectrophotometry, nuclear magnetic resonance, radio-active tracer analysis and X-ray crystallography. In general these procedures are very fast and precise to the point, in some cases, of being able to tell which way a hydrogen atom is spinning. Valuable as they are in terms of results they also share another attribute—high cost. This places many of these new techniques out of the reach of the laboratories of small and even of many medium-size paint companies. There is therefore still a need for developing chemical tests which are available to all.

As part of its program the Paint Laboratory of the Division of Building Research, National Research Council, has a project for the development of new test methods for paint materials and the improvement of existing methods. This work which has formed a substantial part of the laboratory's activities has been of assistance chiefly to the Canadian Government Specifications Board in preparing paint specifications but also is of interest to industrial paint laboratories. During investigation of a method, all available apparatus is used but the final procedure incorporates simple chemical or physical tests wherever possible.

One method that has been examined is the determination of the amount of hydrocarbon diluent in lacquer thinner by means of chemical analysis. Hydrocarbons are inexpensive compared with true nitrocellulose solvents, such as esters and ketones, and latent solvents such as alcohols. There is then a natural tendency for manufacturers to include as much hydrocarbon as possible in lacquer and lacquer thinners. As the proportion of diluent increases the viscosity of the lacquer solution increases, slowly at first but more rapidly as the tolerance limit is neared. Moderate proportions do not have an undesirable effect but when excessive amounts are used the saving in cost per gallon of the thinner is more than offset by the additional thinner required to reduce the lacquer to applicable viscosity. Specifications for lacquer thinners therefore have maximum limits on the amount of hydrocarbon permitted and it is necessary to have an accurate method for this determination.

INITIAL CONSIDERATIONS

In the method developed many years ago lacquer thinner was treated with concentrated sulfuric acid to extract the polar lacquer solvents. The quantity of the remaining solvent was taken to be the total hydrocarbons present in the thinner. This method was probably based on the solubility classification procedures used in organic identification schemes. Hydrocarbons and their halogen derivatives are distinguished from other organic compounds by their insolubility in both concentrated sulfuric and phosphoric acids.

The solubility tests, however, are based on the use of single compounds but lacquer thinners are mixtures. Bogin¹ stated as early as 1941 that toluene is appreciably soluble in mixtures of polar solvents and concentrated sulfuric acid. He recommended that the strength of the acid be reduced to 75%, and when analyzing mixtures containing high proportions of polar solvents to 65%.

The original procedure was modified in a different manner in the method given in the Canadian Government Specifications Board manual for testing paint and related materials.² Instead of reducing the sulfuric acid concentration with water, concentrated phosphoric acid was added. This acid dissolves polar solvents containing up to about nine carbon atoms whereas only the lowest alcohols and ketones are soluble in water. It was evidently thought that the medium boiling lacquer solvents would dissolve in the acid mix while the toluene would be less soluble in the resulting phosphoric-sulfuric-polar solvent mixture.

Although both these modifications are an improvement over the original, neither is completely satisfactory. Diluting the sulfuric acid with water can possibly lead to high results through failure to extract all polar solvents from the hydrocarbons. The phosphoric addition still gives low results at lower concentrations of hydrocarbons. This was illustrated when the procedure was used to recover benzene from mixtures with ethyl acetate with results as shown in *Table 1*.

***Table 1—Recovery of Benzene From Ethyl Acetate
Using Sulfuric-Phosphoric (1:1.7) Extraction***

% Benzene in Mixture	% of Total Benzene Recovered
100	100.
75	92.5
50	88.2
25	50.
10	31.

As can be seen, the recovery declines rapidly with decreasing content of hydrocarbon. Further experiments with benzene showed that a preliminary wash with water significantly increased its recovery from fairly dilute solutions in ethyl acetate, acetone, and methanol.

As a result of the tests with benzene a program to improve the determination of hydrocarbons in lacquer thinners was undertaken. Mixtures of a hydrocarbon with single lacquer solvents were investigated first in the hope of finding a relationship between treatments and the volume of hydrocarbon recovered for the different types of solvents. Different combinations of water washes, diluted acid washes and concentrated acid extractions were tested as well as some water-miscible extrac-

tants. The less satisfactory treatments were discarded and the remainder applied to four different types of lacquer thinners.

MATERIALS AND METHODS

Selection of Materials

Toluene rather than xylene was selected as the test hydrocarbon because toluene is widely used in lacquer thinners. In addition it is highly aromatic so that it might be expected to be partially soluble in the acid mixture. Xylene is not so commonly added to lacquers and because of the two methyl groups attached to the benzene ring is more aliphatic than toluene. Heptane which is similar chemically to the petroleum naphthas often present with toluene in the diluent portion of the thinner was used in two samples. Because it is completely aliphatic heptane was expected to show little tendency to dissolve during the acid extraction.

Two-component mixtures were examined first to see if it was possible to determine the effect of different treatments on the various solvents or groups of solvents. It was then hoped to choose the optimum conditions for the combined solvents, i. e., the lacquer thinners. Mixtures with toluene were made with a water-soluble and a water-insoluble solvent from each chemical group found in lacquers. The mixtures were all made to contain 40% by volume of hydrocarbon. This figure was chosen for two reasons. Most lacquer thinners contain 40 to 60% diluent and, as shown in *Table 1*, there is less difficulty in recovering the hydrocarbon from the higher concentration. It was believed that an improvement at the lower concentration would be reflected at higher levels. Secondly, the two Canadian Government specifications for lacquer thinners both have maximum limits of 40% hydrocarbon content. The mixtures used are given in *Table 2*.

Table 2—Two Component Mixtures

Letter	Hydrocarbon (40%)	Polar Solvent (60% by Volume)	Chemical Type
A	Toluene	Ethanol	Alcohol
B	Toluene	Methyl isobutyl carbinol	Alcohol
C	Toluene	Methyl ethyl ketone	Ketone
D	Toluene	Di-isobutyl ketone	Ketone
E	Toluene	Methyl isobutyl ketone	Ketone
F	Toluene	Ethyl acetate	Ester
G	Toluene	n-Butyl acetate	Ester
H	Toluene	Butyl Cellosolve®	Ether-alcohol
I	Heptane	Methyl ethyl ketone	Ketone

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HYDROCARBONS IN LACQUER THINNERS

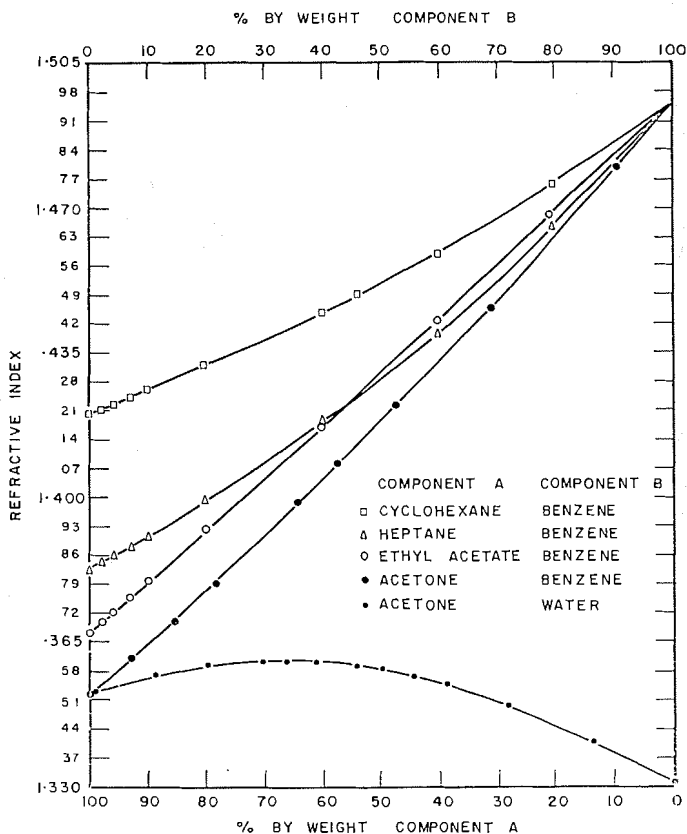


Figure 1—Refractive index vs. composition

Refractive index was chosen as the method for determining the concentration of hydrocarbon remaining after treating the above mixtures by the various procedures being investigated. The refractive indices of each component and of the resultant mixture were measured. Although only three points were available for each combination the graphs were plotted as straight lines. It was concluded that this construction was valid after consideration of *Figure 1* which was based on benzene-solvent mixes having much greater variation in percentage composition than the toluene mixtures. It can be seen that it is only where the solvents are similar chemically, e.g. benzene-cyclohexane and benzene-heptane, or exhibit association or hydration, e.g. acetone-water, that the plot departs appreciably from linearity. Compositions calculated on a percent by volume basis which was used in the present work would have yielded more nearly linear lines, except for acetone-water.

Procedure

After preparation, the solvent mixtures were treated to determine the best method for recovering the optimum volume combined with the maximum purity of hydrocarbon. All but one of the methods consisted of extracting 50 ml of mixture with different amounts or concentrations of water and acid or other solvents. After extraction, the remaining hydrocarbon was twice washed with an equal volume of water to remove any residual acid and the volume of recovered material measured in 25-ml stoppered graduated cylinders. The refractive index was taken and the amount of hydrocarbon in the material obtained from the appropriate refractive index-percent composition graph. Drying some samples with anhydrous sodium sulfate had no effect on the refractive index so it was concluded that there was a negligible amount of water in the isolated hydrocarbon.

Fifty-ml samples were pipetted into the separatory funnels so that the ideal recovery would be 20 ml. Larger volumes indicate that not all the lacquer solvent was extracted from the hydrocarbon while smaller volumes, which were the usual result, indicate that some of the hydrocarbon dissolved in the acid-polar solvent mix.

One procedure suggested by an industrial paint laboratory was different in that the Babcock bottle used for butter fat determinations was employed in place of several extractions in a separatory funnel. In this method 5 ml of sample were pipetted into the bottle which contained 30 ml of concentrated sulfuric-phosphoric acid mix (1:1:7). After shaking, more acid was added until the undissolved hydrocarbon rose into the graduated neck where the volume was read. A few drops of the recovered material was used to measure the refractive index.

The acids used in preparing the extraction mixtures were concentrated (96%) sulfuric acid which is 18 Molar in strength and concentrated (85%) phosphoric acid which is 14.6M. The standard mix of 170 parts phosphoric to 100 parts sulfuric yields a solution 6.7M in the latter and 9.2M in the former. Molar concentrations have been used to show more clearly the dilution by volume of these acids.

TESTS AND RESULTS

Effect of Water Washes

The first experiments were carried out on alcohol-toluene and ketone-toluene mixtures to see whether preliminary water washes would aid in recovering toluene from water-insoluble solvents. In reporting results the less satisfactory procedures have been omitted because of the large number of possible combinations. The different procedures used and the volumes recovered are shown in *Table 3*.

In all cases except one, the preliminary water washes were an improvement over direct treatment with the acids even with the more

**Table 3—Recovery of Toluene from Toluene-Alcohol
And Toluene-Ketone Solutions**

Method Number	First Wash	Second Wash	Acid Treatment
1	None	None	50 ml (6.7M H_2SO_4 (9.2M H_3PO_4)
2	50 ml H_2O	None	50 ml "
4	50 ml H_2O	50 ml H_2O	50 ml "
6	60 ml H_2O	50 ml H_2O	50 ml "
10	75 ml H_2O	50 ml H_2O	50 ml "
11	100 ml H_2O	50 ml H_2O	50 ml "

Method Number	Volume ml	Purity %	% Toluene Recovered	Volume ml	Purity %	% Toluene Recovered
		Mixture A (Ethanol-Toluene)			Mixture B (MIBC-Toluene)	
1	19.0	99.1	94.1	13.1	96.3	63.1
2	19.4	99.2	96.2	14.2	95.6	67.9
4	19.0	99.2	94.2	14.6	96.3	70.3
6*	19.45	99.45	96.7	14.8	97.0	71.8
11	18.0	100.0	90.0	14.8	98.4	72.8

		Mixture C (MEK-Toluene)			Mixture E (MIBK-Toluene)	
1	18.6	96.6	89.8	17.5	94.5	82.9
2	19.2	97.5	93.6	18.1	92.9	84.0
4	18.9	97.5	92.1	17.8	92.7	82.5
6*	19.65	99.15	97.4	17.9	94.2	84.3
10	19.2	97.5	93.6	18.1	93.0	84.1
11*	19.35	99.1	95.9	18.1	94.5	85.5

* Mean of two runs.

water-insoluble solvents. The larger volumes were generally better than one or two 50-ml washes.

Effect of Diluted Acid Wash

In this group of tests diluted acid mixture was used as a wash before the concentrated acid extraction, either as a replacement for or in combination with the water wash. The concentrated mix was diluted with an equal volume of water to provide the preliminary wash. Methods and results are shown in *Table 4*.

Comparison with *Table 3*, Method 2 vs. 8, shows that the diluted acid was slightly better when used in place of a single water wash. Method

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7 which had both a water and a diluted acid wash was better than both the corresponding two water washes (No. 4) and a single acid wash (No. 8). The amount of water to be used was then determined at two volume levels of diluted acid as given in *Table 5*.

At both quantities of water, the larger volume of diluted acid generally gave better results. With 50 ml of acid, the larger volume of water gave better results with water-soluble solvents and poorer results with water-insoluble solvents. However, the combination of 100 ml water and 100 ml diluted acid was the best all-round procedure. The volume of heptane was near the theoretical with the two methods shown here, so this mixture was not tested further. Even the best methods gave a poor recovery of toluene from di-isobutyl ketone (DIBK). With the other

Table 4

Method Number	Water Wash	Second Wash	Acid Treatment
7	50 ml	50 ml (3.3M H_2SO_4 (4.6M H_3PO_4)	50 ml (6.7M H_2SO_4 (9.2M H_3PO_4)
8	None	50 ml "	50 ml "

Solvent Mixture	Volume ml	Method 7 Purity %	% Toluene Recovered	Volume ml	Method 8 Purity %	% Toluene Recovered
A	19.4	99.9	96.9	19.2	99.2	95.2
B	15.4	97.3	74.9	14.9	95.8	71.4
C	19.1	99.8	95.3	19.2	98.5	94.5
E	18.0	95.3	85.8	18.3	93.2	85.3
F	19.4	94.8	91.9	19.2	94.9	91.1
G	16.6	89.0	73.9	16.2	88.2	71.5
I	20.0	97.1	97.1	19.4	98.7	95.7

Table 5

Method Number	Water Wash	Second Wash	Acid Treatment
7	50 ml	50 ml (3.3M H_2SO_4 (4.6M H_3PO_4)	50 ml (6.7M H_2SO_4 (9.2M H_3PO_4)
14	50 ml	100 ml	50 ml
15	100 ml	50 ml	50 ml
16	100 ml	100 ml	50 ml

Solvent Mixture	Volume ml	Method 7		Volume ml	Method 15	
		Purity %	% Toluene Recovered		Purity %	% Toluene Recovered
A	19.4	99.9	96.9	19.8	100.0	99.0
B	15.4	97.3	74.9	15.0	97.9	73.4
C	19.1	99.8	95.3	19.2	99.5	95.5
D	—	—	—	7.8	78.6	29.9
E	18.0	95.3	85.8	17.2	95.4	82.0
I	20.0	97.1	97.1	—	—	—

Solvent Mixture	Volume ml	Method 14		Volume ml	Method 16	
		Purity %	% Toluene Recovered		Purity %	% Toluene Recovered
A	19.6	100.0	98.0	19.6	99.9	97.9
B	15.8	97.8	77.3	15.8	97.9	77.3
C	19.5	99.6	97.1	19.5	99.4	96.9
D	7.2	74.0	26.6	8.2	78.5	32.2
E	18.0	95.4	85.9	18.2	99.8	90.8
F	19.4	96.9	94.0	19.6	98.0	96.0
G	17.4	90.2	78.5	17.6	88.5	77.9
H	17.8	99.5	88.6	18.6	99.7	92.7
I	19.9	98.0	97.5	—	—	—

methods three layers were usually formed upon addition of the concentrated acid mixture.

The best diluted acid procedure, No. 16 (*Table 5*) can be compared with the best water method, No. 6 (*Table 3*). In every case except one the diluted acid procedure is better with regard to either the volume recovered or the purity of the toluene. Both methods were reserved for further work on the lacquer thinners.

Effect of Acid Composition of Second Wash

The proportions of sulfuric and phosphoric acids in the diluted acid extractions and the amounts of the mixtures added were varied. A definite trend could not be detected due, perhaps, to the strong interaction

between treatments. Two procedures which could not separate toluene from methyl isobutyl carbinol (MIBC) were abandoned and the remaining five variations retained for application to lacquer thinners.

Effect of Concentrated Acid Composition

Since preliminary water and diluted acid treatments had been effective with concentrated acid mixture it was decided to apply the same technique to the concentrated sulfuric acid of the original procedure. It was thought that sulfuric acid might be better with the water-insoluble solvents. Polar solvents tend to become more insoluble in 85% (14.6M) H_3PO_4 with increasing chain length, the limit being about nine carbon atoms in the molecule. The comparison was made using three different preliminary acid washes as shown in *Table 6*.

In all cases except one the acid mixture was much superior to the

Table 6

Table 6

Method Number	Water Wash	Second Wash	Acid Treatment
21	100 ml	100 ml 9M H ₂ SO ₄	50 ml 18M H ₂ SO ₄
22	100 ml	100 ml 9M H ₂ SO ₄	50 ml (6.7M H ₂ SO ₄ 9.2M H ₃ PO ₄)
26	100 ml	100 ml 12M H ₂ SO ₄	50 ml 18M H ₂ SO ₄
25	100 ml	100 ml 12M H ₂ SO ₄	50 ml (6.7M H ₂ SO ₄ 9.2M H ₃ PO ₄)
23	100 ml	100 ml 14.6M H ₃ PO ₄	50 ml 18M H ₂ SO ₄
24	100 ml	100 ml 14.6M H ₃ PO ₄	50 ml (6.7M H ₂ SO ₄ 9.2M H ₃ PO ₄)

Method Number	Volume ml	Purity % Mixture A	% Toluene Recovered	Volume ml	Purity % Mixture B	% Toluene Recovered
21	13.4	99.6	67.2	28.	—	—
22	19.3	100.0	96.5	36.	—	—
26	13.5	99.9	67.4	15.2	91.3	69.4
25	19.4	100.0	97.0	15.7	96.1	75.4
23	5.7	—	—	38.	—	—
24	19.2	99.8	95.8	15.4	97.1	74.8

	Mixture C			Mixture E		
21	13.4	99.9	66.9	9.4	98.3	46.2
22	19.5	99.8	97.3	19.2	98.7	94.8
26	15.6	99.6	77.7	14.2	99.7	70.8
25	19.0	99.9	94.9	18.2	99.7	90.7
23	14.0	99.8	69.9	11.0	99.6	54.8
24	19.2	99.8	95.8	17.0	99.5	94.5

Table 7

Method Number	Water Wash	Second Wash		Acid Treatment	
29	100 ml	100 ml	(3.3M H_2SO_4 (4.6M H_3PO_4)	75 ml	(6.7M H_2SO_4 (9.2M H_3PO_4)
31	100 ml	100 ml	"	75 ml	(4.5M H_2SO_4 (11.M H_3PO_4)

Solvent Mixture	Volume ml	Method 29 Purity %	% Toluene Recovered	Volume ml	Method 31 Purity %	% Toluene Recovered
A	19.5	99.8	97.3	19.3	99.9	96.4
B	17.0	96.9	82.4	14.5	99.4	72.1
C	19.0	99.9	94.9	19.2	99.8	95.8
D	10.4	80.5	41.9	49.	—	—
E	18.0	96.0	86.4	18.6	95.5	88.8
F	19.6	98.7	96.7	20.4	97.7	99.7
G	18.4	89.9	82.7	18.7	87.5	81.8
H	18.4	99.9	91.9	18.2	99.7	90.7

straight sulfuric acid. Sulfuric acid reduced 50% by volume and straight phosphoric acid were both somewhat unsatisfactory for preliminary washes before extracting with the acid mixture.

Tests were next made in the other direction, i.e. with increasing proportions of phosphoric acid at two volume levels as shown in *Tables 7* and 8.

The increased phosphoric acid was better with some of the water-soluble solvents and ketones but poorer with the alcohols. It did not separate toluene from di-isobutyl ketone (DIBK) and yielded a slightly high volume with ethyl acetate. In the next series a method with an intermediate phosphoric acid composition was included to see whether an optimum content might be reached.

Method 17 was dropped because it gave high results with MIBC without a corresponding increase in the yield from other solvents. Method 36 did not seem to be an improvement over similar methods and since it was the last procedure developed it was not tried on the lacquer thinner combinations.

Effect of Concentrated Acid Volume

The other variable of acid extraction, the volume, was also explored. Results for these methods, except the Babcock procedure, No. 37, have already been reported but are listed again for ease of comparison. In *Table 9* the readings from the Babcock bottle have been converted to millilitres recovered from 20 ml toluene in the sample.

Table 8

Method Number	Water Wash	Second Wash		Acid Treatment	
17	100 ml	100 ml	(3.3M H_2SO_4 (4.6M H_3PO_4)	100 ml	(6.7M H_2SO_4 (9.2M H_3PO_4)
36	100 ml	100 ml	"	100 ml	(5.6M H_2SO_4 (10.M H_3PO_4)
32	100 ml	100 ml	"	100 ml	(4.5M H_2SO_4 (11.M H_3PO_4)

Solvent Mixture	Method 17		Method 36		Method 32	
	Volume ml	% Toluene Recovered	Volume ml	% Toluene Recovered	Volume ml	% Toluene Recovered
A	19.6	97.7	19.3	96.3	19.6	97.8
B	21.4	87.2	16.3	75.8	15.7	77.4
C	19.0	85.7	19.4	96.8	19.2	95.9
D	11.5	57.4	4.6	—	48.	—
E	18.8	92.4	18.5	89.4	18.5	89.4
F	—	—	19.4	96.6	20.2	99.9
G	—	—	19.4	95.9	19.6	89.6
H	—	—	17.6	84.9	18.4	91.7

An obvious trend can be seen in that the larger volumes of concentrated acid gave better results with water-insoluble solvents and the smaller volumes better results with water-soluble solvents. This was especially true of the Babcock method, No. 37, which yielded results with the water solubles that were as low as the first sulfuric-phosphoric procedure, No. 1, while with DIBK it was the only method to approach the theoretical yield of 20 ml. It could not be predicted which solvent effect would predominate when analyzing a lacquer thinner so methods 16, 29, and 37 were selected for trials.

Effect of Solvent Extractions

A different approach to recovering toluene from solvent mixes was attempted by the use of a water-miscible solvent extraction before the concentrated acid extraction. It had been suggested that a solvent such as ethanol might cause some of the polar lacquer solvents to dissolve in the water phase. The toluene in the remaining thinner would then be present in a higher proportion and when extracted with acid would have less tendency to dissolve in the acid-polar solvent mixture. Fifty percent ethanol-water was used at two volume levels but except with DIBK gave lower recoveries than the corresponding water washes, especially with the water-soluble solvents. This is probably due to the coupling action of ethanol on toluene-water mixtures.

The concept was then developed of using a material in which lacquer solvents but not toluene are soluble. Ethylene glycol was chosen although preliminary tests showed that it did not dissolve DIBK. Twenty-five per-

Table 9

Method Number	Water Wash	Second Wash		Acid Treatment		
16	100 ml	100 ml	(3.3M H_2SO_4 (4.6M H_3PO_4)	50 ml	(6.7M H_2SO_4 (9.2M H_3PO_4)	
29	100 ml	100 ml	"	75 ml	"	
17	100 ml	100 ml	"	100 ml	"	
37	None	None		Large excess	"	

Solvent Mixture	Volume ml	Purity %	% Toluene Recovered	Volume ml	Purity %	% Toluene Recovered
		Method 16			Method 29	
A	19.6	99.9	97.9	19.5	99.8	97.3
B	15.8	97.9	77.3	17.0	96.9	82.4
C	19.5	99.4	96.9	19.0	99.9	94.9
D	8.2	78.5	32.2	10.4	80.5	41.9
E	18.2	99.8	90.8	18.0	96.0	86.4
F	19.6	98.0	96.0	19.6	98.7	96.7
G	17.6	88.5	77.9	18.4	89.9	82.7
H	18.6	99.7	92.7	18.4	99.9	91.9

	Method 17			Method 37		
	Volume ml	Purity %	% Toluene Recovered	Volume ml	Purity %	% Toluene Recovered
A	19.6	99.7	97.7	19.1	99.8	95.3
B	21.4	81.5	87.2	17.5	99.4	87.0
C	19.0	90.2	85.7	18.4	99.7	91.7
D	11.5	99.9	57.4	18.4	89.7	82.7
E	18.8	98.3	92.4	18.0	99.6	89.6
F	—	—	—	19.2	99.9	95.9
G	—	—	—	19.0	97.7	92.8
H	—	—	—	18.0	99.9	89.9

cent water was added to the glycol to ensure formation of two phases. This solution was tested as a replacement for the water wash and the diluted acid wash but was inferior to both. Finally 1:1 and 2:1 mixtures of ethylene glycol-ethanol were used with addition of water if required to form two layers. Here again the recoveries were quite low. None of the solvent extraction procedures were applied to the composite thinners.

Analysis of Lacquer Thinners

Four different types of lacquer thinners representing the various types in common use were formulated. Formula J, "High Quality" and Formula L, "Low Quality" were based on information given in Mattiello³ with adjustment of the hydrocarbon content down to 40%.

Table 10—Formulas of Lacquer Thinners

	Formula J High Quality	Formula L Low Quality
n-Butyl acetate	25	20
Ethyl acetate	10	15
n-Butanol	15	10
Ethanol (95%)	10	15
Toluene	40	20
Heptane	—	20
Parts by volume	100	100

	Formula K High Solids	Formula M High-Low
n-Butyl acetate	20	—
Ethyl acetate	5	—
Acetone	—	15
Methyl ethyl ketone	25	15
Di-isobutyl ketone	—	20
n-Butanol	10	—
Methyl isobutyl carbinol	—	5
Isopropanol	—	5
Toluene	40	40
Parts by volume	100	100

**Table 11—Procedures for Isolating Hydrocarbons
From Lacquer Thinners**

Method Number	Water Wash	Second Wash	Acid Treatment
1	None	None	50 ml (6.7M H ₂ SO ₄ (9.2M H ₃ PO ₄)
6	60 ml	50 ml H ₂ O	50 ml "
16	100 ml	100 ml (3.3M H ₂ SO ₄ (4.6M H ₃ PO ₄)	50 ml "
25	100 ml	100 ml 12M H ₂ SO ₄	50 ml "
30	100 ml	100 ml 12M H ₂ SO ₄	75 ml "
29	100 ml	100 ml (3.3M H ₂ SO ₄ (4.6M H ₃ PO ₄)	75 ml "
32	100 ml	100 ml "	100 ml (4.5M H ₂ SO ₄ (11.1M H ₃ PO ₄)
33	100 ml	100 ml 14.6M H ₃ PO ₄	75 ml (6.7M H ₂ SO ₄ (9.2M H ₃ PO ₄)
37	None	None	Large excess "

Formula K, "High Solids" was obtained from commercial literature⁴ with adjustment of toluene up to 40%. Formula M, "High-Low" was also a commercial formula⁵ with the toluene content increased to 40% and di-isobutyl ketone used in place of the suggested ethyl amyl ketone.

The composition of the four thinners used in this work is given in *Table 10* and the details of the different procedures applied to them in *Table 11*. The direct concentrated acid extraction No. 1, is included for comparison. The complete test results are shown in *Table 12*.

The "High-Low" thinner reacted quite differently from the others and the Babcock procedure, No. 37, appears to be the only acceptable one for this type of thinner. However, with the more customary thinners method 37 is worse than all the extraction procedures tested except the original method. The mean volume recovered, mean purity, and mean percent hydrocarbon recovered were calculated for each method from the first three thinners. These values are given in *Table 13*.

Method 32 gave high total volume with all four thinners and was

Table 12—Recovery of Hydrocarbons from Four Lacquer Thinners

Method Number	Volume ml	Purity %	% Toluene Recovered	Volume ml	Purity %	% Hydro- carbon Recovered
		Formula J			Formula L	
1	17.8	91.7	81.6	19.5	91.4	89.1
6	19.3	97.5	94.1	19.6	95.1	93.2
16	19.8	95.1	94.1	19.0	99.5	94.5
25	19.4	99.0	96.0	19.2	98.1	94.2
29	19.8	95.7	94.7	19.3	96.5	93.1
30	19.4	98.6	95.6	19.8	96.5	95.5
32	20.4	94.0	95.9	20.2	93.7	94.6
33	18.8	97.8	91.9	19.6	96.8	94.9
37	18.1	98.8	89.4	19.2	95.6	91.8

Formula K				Formula M		
1	18.6	92.6	86.1	—	—	—
6	19.4	96.7	90.7	22.2	88.5	98.2
16	19.8	99.5	95.7	24.4	—	—
25	19.6	99.5	97.5	20.6	92.0	94.8
29	18.8	99.7	93.7	18.8	95.0	89.3
30	19.4	98.6	95.6	22.2	84.2	93.5
32	20.1	94.0	94.5	28.	—	—
33	20.2	96.1	97.1	21.2	91.4	96.9
37	18.5	99.6	92.1	19.5	95.5	93.1

Table 13

Method Number	Total Volume Recovered	Purity %	% Hydrocarbon Recovered
1	18.63	91.9	85.6
6	19.43	95.4	92.7
16	19.53	97.1	94.8
25	19.4	98.9	95.9
29	19.3	97.3	93.8
30	19.53	97.9	95.6
32	20.23	93.9	95.0
33	19.53	96.9	94.6
37	18.6	98.0	91.1

rejected. In specification testing of maximum limits it is necessary to err on the low side. With thinners J, K, and L, methods 16, 30, and 33 gave the highest total recovered volume. However, the mean from 33 is misleading because of the high result obtained with K. In percent hydrocarbon recovered, which includes both the purity and amount of isolated solvent, methods 25, 30, and 16 rank in that order. No. 30 has the best over-all rating, i.e., high recovered volume and high purity.

One surprising feature is the small difference between the various extraction procedures when applied to the thinners as compared to the results on the two-component mixtures. For example, No. 16 gave considerably better yields than No. 6 with several simple mixes but the difference between them on the thinners is very small.

SUMMARY

Study of the results from the two-component mixtures showed that the sulfuric acid content of the concentrated extraction mixture seemed to be the most important variable. There was not an exact correlation, partly because there were no experiments with acid mixes between straight 18M H_2SO_4 and the combination of 6.7M H_2SO_4 and 9.2M H_3PO_4 . This trend, however, did not appear in the lacquer thinner results.

It was also impossible to choose optimum conditions for combined solvents by studying the two component mixtures. There was not one solvent or group of solvents that correlated with the order of results obtained with the lacquer thinners. The preliminary tests, therefore, served only to eliminate some of the more unsatisfactory procedures.

It is doubtful whether the method given in U.S. Federal Specification TT-T-266 would extract all the water-insoluble ketones and alcohols. The procedure, in paragraph 4.2.5.3 of the specification, makes one extraction with concentrated phosphoric acid. In the work reported here, methods 24 and 33 had H_3PO_4 as a wash prior to extraction with the

sulfuric-phosphoric mix. In spite of this more severe treatment, method 33 yielded high results with two of the four thinners which indicates incomplete extraction of lacquer solvents.

From the lacquer thinner results it is concluded that the procedure using the Babcock bottle is the only suitable chemical method for thinners containing large quantities of polar solvents that have eight or more carbon atoms. Generally such materials are only present to any extent in "High-Low" lacquer thinners. It is also concluded that the same procedure is unsatisfactory for analyzing the customary type of lacquer thinner.

For conventional thinners the method outlined below gave the most consistent results in volume and purity of the recovered hydrocarbon. The latter property is important if the isolated material is to be subjected to further examination. The procedure is as follows:

50 ml of thinner is pipetted into a separatory funnel and washed with 100 ml of water. The water layer is removed and 100 ml of 75% H_2SO_4 (2:1) added. The funnel is shaken gently, allowed to cool and the acid layer drawn off 75 ml of concentrated phosphoric-sulfuric acid mix (1.7:1) is added, shaken and discarded as before. The remaining solvent is washed twice with an equal volume of water. The washed hydrocarbon is transferred to a stoppered graduated cylinder and the measured volume multiplied by 2 to obtain the percent hydrocarbons by volume.

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