California Research Corporation

O.Z. 14487
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117001463
Ludwigshaven Nov. 30, 1943

TOM MICROFILM NO. 19

PROCESS FOR OBTAINING PURE m-XYLENE

The direct production of pure m-xylene from mixtures of isomeric xylenes is very difficult. It has therefore been proposed to sulfonate the xylenes in these mixtures and to separate the sulfonic acids of the isomeric xylenes by fractional crystallization, and then to split these hydrolytically. This process, however, is complicated and difficult to perform technically. The ease with which m-xylene can be sulfonated has therefore been utilized by taking limited amounts of an aqueous sulfuric acid (an 80% acid), separating the resultant m-xylene sulfonic acid from the unsulfonated constituents, and then hydrolytically splitting the product into m-xylene by heating with water. In this manner a strongly enriched but not pure m-xylene is obtained since it is hardly possible to avoid that small portions of the other isomers are also sulfonated. In this process the solid m-xylene sulfonic acid was first left to crystallize.

It has now been found that pure xylene can be obtained from such mixtures in a technically simple manner when the mixtures are first treated with a sulfonating agent in the known manner and the sulfonation mixture is split with steam, without separation of the unconsumed sulfuric acid. It has been found that m-xylene sulfonic acid is more readily split hydrolytically than the sulfonic acids of the isomeric xylenes and that by maintaining definite temperatures it becomes possible to practically split only the m-xylene sulfonic acid. For example, if much steam is passed through the sulfonation mixture the m-xylene sulfonic acid can be split as low as at 123°C. In order to save steam the operation is best conducted at about 135 to 145°C, preferably between 140 and 142°. The splitting of the p-xylene sulfonic acid then takes place at a temperature of about 150° and that of the o-xylene sulfonic acid or of the ethyl benzene sulfonic acid, which is isomeric with the xylene sulfonic acid, at about 180°. Some water is preferably added to the reaction mixture. The splitting temperatures are to some extent dependent on the prevailing pressure; the operation can be conducted at ordinary, or increased, or reduced pressure.

The starting mixture may be industrial coke oven xylene which, in addition to the three isomeric xylenes, also contains paraffinic and olefinic hydrocarbons. Altho these aliphatic hydrocarbons do not disturb the separation, they are preferably removed to the major extent, for example, by azeotropic distillation, in order to concentrate the m-xylene in the mixture and to prevent an unnecessary dilution of the sulfuric acid before sulfonation.

The sulfonation can be done with conc. sulfuric acid in which case the three xylene isomers are sulfonated. It is however better to work with aqueous, say an 80% sulfuric acid since, regardless of the sulfonation of any olefins present, m-xylene is then mainly sulfonated. By operating in this manner the non-sulfonated portion of the mixture takes up the other xylene isomers together with only small amounts of m-xylene. The sulfonation is preferably performed with twice the amount of 80% sulfuric acid, referred to the hydrocarbon mixture, at about 70°C and with good agitation. After sulfonation the acid layer is separated, is diluted with about ten vol.% of water and superheated steam is introduced at increasing temperature in sufficient amounts to prevent cracking of hydrocarbons or reduction of sulfuric acid. After recovering a small amount of first runnings containing olefinic constituents and their cracking products together with m-xylene, the desired hydrolysis takes place at 140-142° at high velocity, and distillate is recovered as long as the portion of oil is greater than the portion of water. The resulting oil consists almost entirely of pure m-xylene. The resulting m-xylene contains less than 1% of impurities, chiefly p-xylene; it is freed from acidic products by washing with water. The distillation residue may be treated with steam at high temperatures and sulfonic acids of p- and o- xylene may eventually be fractionally separated in which case, as has been mentioned, p-xylene sulfonic acid breaks down at about 150° and o-xylene sulfonic acid at about 180°. When the sulfonation has been done with 80% sulfuric acid alone, only a small amount of the other xylene isomers are recovered from the distillation residue.

The sulfuric acid can be almost entirely recovered by distilling with steam at increasing temperature until oil no longer comes over. The acid which then remains as residue, eventually after separation of tarry constituents which are chiefly formed when the starting material contains olefinic hydrocarbons, is concentrated in the conventional manner to 80% acid.

Example

500 pts. (vol) of coke oven xylene(b.P. 137-142°C, D_{20} 0.842), containing eleven % of paraffinic and naphthenic hydrocarbons (Br No 6.2 g/100 cc)

is stirred with 950 pts (vol) of 79% sulfuric acid for 9 1/2 hours at 70°. The remaining unsulfonated portion (320 pts. vol) is withdrawn. The central and lower layer consisting of 1030 pts. (vol) is diluted with 150 pts. (vol) of water and heated to 130°C, whereupon steam superheated to about 140° is passed through. The first portions of the distillate up to 140° are separated as first runnings. They consist of small amounts of m-xylene together with low boiling cracking products. Decomposition of the m-xylene sulfonic acid then takes place very rapidly. The portions coming over at a still temperature of 140-142° are recovered as the main fraction, for which the amount of oil is larger than the amount of water. The following fractions are obtained:

Fraction	Still temperature	pts (vol) of total distillate	the distillate consists of Pts(vol) of oil	pts(vol)of water
First runnings	136-140°C	11	9	2
Main fraction	140-142°C	137	112	25
After-runnings	142-187°C	257	29	228

Of the sulfonated 180 pts (vol), 150 pts (vol) are consequently recovered in the splitting reaction, of which 112 pts (vol) are pure m-xylene. The tarry residue in the sulfuric acid amounts to 16 pts (wt). The distillationresidue consists of 1143 pts (vol) of 69.13% sulfuric acid which, after consentration to 79-80%, can be used again.

Claim

Process for producing m-xylene from hydrocarbon mixtures containing it, by sulfonation and subsequent hydrolytic splitting of the xylene sulfonic acids, characterized in that steam is passed through the sulfonation mixture, without separation of unconsumed sulfuric acid, at a temperature such that only the m-xylene sulfonic acid is split hydrolytically.

STANDARD OIL DEVELOPMENT COMPANY

Methods Used by I.G. at Oppau
Described by Dr. Stern at an Analytical Conference, Berlin, 1940
Reel 21, Pages 631-700

PROCEDURE FOR THE ANALYSIS OF PENTENE AND HEXENE FRACTIONS IN A V-TUBE (1)

Group I x · = ! - · (Isobutylene Group)(2)

Determine bromine number according to McIlhiney.

Wash the V-tube with water, evacuate, weigh, add 4.5 N HBr (8 times the volume of liquid hydrocarbon), shake for 1.5 hour, separate the HBr, wash with water until no longer acid, drain water thoroughly, weigh the tube. The hydrocarbons are distilled off (pentane 70°C., hexane 90°C.) from one arm to the other (0°C.). Withdraw residue by suction and weigh the tube. This 4.5 N HBr treatment is repeated until the hydrocarbon removal is less than 5% by weight.

Saturated Hydrocarbons x - x - x

Determine bromine number according to McIlhiney.

Treat with concentrated HBr at 0°C. (5 times the volume of hydrocarbons), shake for 2 hours, and separate the acid layer.

The hydrocarbons containing the bromides are collected in one of the side arms, the middle arm is partly filled with 1:1 KOH solution, let stand overnight to absorb gaseous HBr, the KOH is removed and the tube weighed.

The bromine number of the hydrocarbon-bromide mixture is obtained to determine the extent of the HBr reaction. Distill the hydrocarbon-bromide mixture from one side arm (pentane 70°C., hexane 90°C.) to the other, cool to 0°C. The distillate is collected in the middle arm and sucked out while the bromide mixture is kept at 0°C. The suction is continued to remove hydrocarbon vapors until the tube's weight remains constant.

Group II . = . - ! - x (Isopropylethylene Group)

Add water to the bromide mixture in the tube. Shake, separate, and repeat addition until the water is no longer acid. Titrate the HBr in the water washes.

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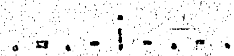
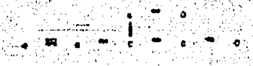
(1) After removal of dienes (page 6) and peroxides.

(2) Michael and Leopold. Liebig Ann. Chem., 379, 288, 297.
Michael and Zeidler. " " " , 385, 252, 269.

Factor for  2

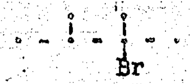
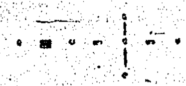
 2,5

 4

 10

Determine bromine number according to McIlhiney in the residual bromides, if olefins are again formed, then members of Group IIIa are present.

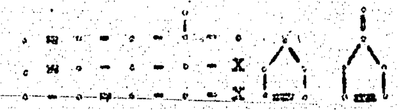
<u>Group IIIa</u>  (Tertiary butyl ethylene group)

The  90%(1) of which is formed from 

is transformed into  on treatment with water even at room temperature (retro-pinacoline rearrangement).

Group IIIa has so far never been found in cracked gasolines.

Group III occurs in diisobutylenes.

<u>Group III.</u> 

The amount of normal C chains is determined from the bromine content of the remaining hydrocarbons. We use about 10 ml. for the analysis when a 150-ml. side arm V-tube is used. Smaller V-tubes are used for small samples.

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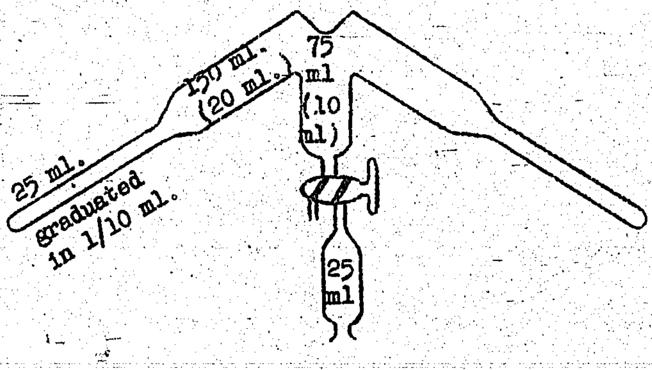
(1) See Dnlacre C 1906 II 498.



V-TUBE FOR OLEFIN DETERMINATION

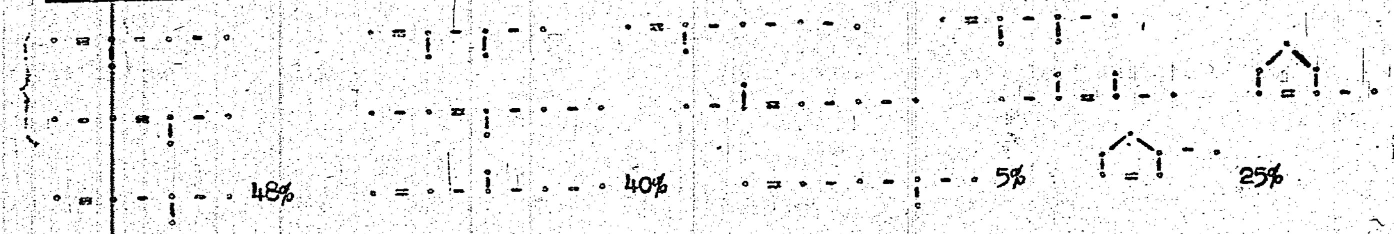
Data in parentheses are for the micro size; other data for the larger form of the apparatus.

SEPARATION AND DETERMINATION OF DIENE-FREE HYDROCARBON MIXTURES

Group Pentenes Hexenes

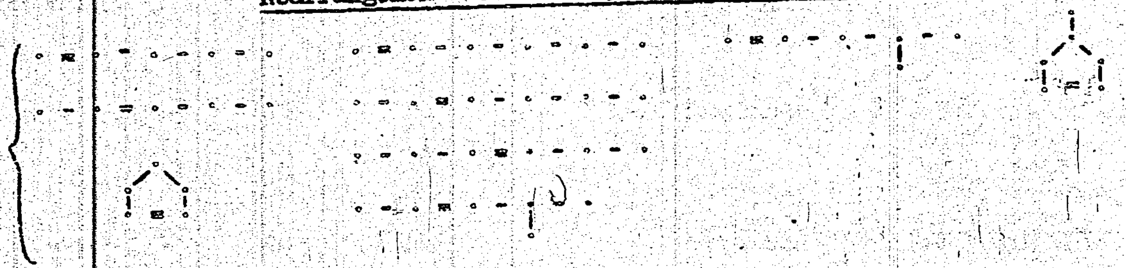
I
4.5 N HBr

II
8.5 N HBr

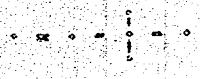
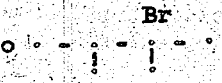


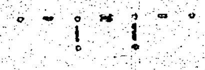
Rearrangement to Tertiary Bromides (Michael's Rearrangement)

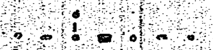
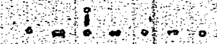
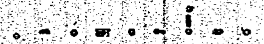
III



IV

 90% rearrangement to 

with H_2O at 40°C. changes to 

Olefin	Br No., McIlhiney				Reaction with 4.5 N HBr	Gives at 0°C. Neut. $KMnO_4$ in Excess
	Addition		Substitution			
	Calc.	Found	20°	40°		
Trimethylethylene (1) 	228	220	30	35	Soluble	Acetone Acetic acid
Assym. methylethylethylene 	228				Soluble	Methylethylketone Lit.
Isopropylethylene (1)	228	225	26	93	Insoluble	Isobutyric acid
Isohexene (1) 	190				Insoluble	Isovalerianic acid Oxalic acid
Active methylcyclopentene (1) 	195	190	55	180	Insoluble	
Hexene-1 	190				Insoluble	n-Valerianic acid Formic acid Oxalic acid
Hexene-2 	190				Insoluble	n-Butyric acid acetic acid
Hexene-3 	190				Insoluble	Propionic acid
Sym. methylisopropylethylene 	190	180	15	70	Insoluble	Isobutyric acid Acetic acid
Sym. methylcyclopentene  (1)	195				Insoluble	
Tert. isobutylethylene (1) 	190				Insoluble	Trimethyl acetic acid Oxalic acid

(1) Synthetically prepared according to the literature.

Olefin	Br No., McIlhiney Addition Calc.	Found	Substitution 20°	40°	Reaction with 4.5 N HBr	Gives at 0°C. Neut. KMnO4 in Excess	
Trimethylethylene (1)	228	220	30	35	Soluble	Acetone Acetic acid	
Assym. methylethylethylene	228				Soluble	Methylethylketone	Lit.
Isopropylethylene (1)	228	225	26	93	Insoluble	Isobutyric acid Oxalic acid	
Pentene-1 (1)	228				Insoluble	N-butyric acid Oxalic acid Formic acid	Not succinic acid as given in the lit.
Pentene-2 (1)	228	227	6	5	Insoluble	Propionic acid Acetic acid	
Cyclopentene (1)	236	235	15	20	Insoluble	Glutaric acid	
3-Methylpentene-2 (1)	190				Soluble	Not tested	
2-Methylpentene-2	190				Soluble	Not tested	
Tetramethylethylene (1)	190	190	20	35	Soluble (repeated treatment)	Not tested	The tertiary alcohol decomposes at room temp. into H_2O and olefin in the presence of acids. The pure olefin will slowly add H_2O on standing.
Assym. diethylethylene (1)	190	175	60	75	Soluble		
Assym. methylpropylethylene	190				Soluble		
Assym. methylisopropylethylene	190				Soluble		
Tertiary methylcyclopentene (1)	195	194	68	80	Polymerizes		
3-Methylpentene-1 (1)						Ethylmethyl acetic acid, oxalic acid	
Isohexene (1)	190				Insoluble	Isovalerianic acid Oxalic acid	
Active methylcyclopentene (1)	195	190	55	180	Insoluble		
Hexene-1	190				Insoluble	n-Valerianic acid Formic acid Oxalic acid	
Hexene-2	190				Insoluble	n-Butyric acid acetic acid	
Hexene-3	190				Insoluble	Propionic acid	
Sym. methylisopropylethylene	190	180	15	70	Insoluble	Isobutyric acid Acetic acid	
Sym. methylcyclopentene (1)	195				Insoluble		
Tert. isobutylethylene (1)	190				Insoluble	Trimethyl acetic acid Oxalic acid	

(1) Synthetically prepared according to the literature.

Determination of Dienes

Sample: Fraction up to 120°C.

Procedure:

1. Br No. According to McIlhiney
Determination of Dienes (with Conjugated Double Bonds)

(a) Cyclic: Addition of α-naphthoquinone (1% by weight) with strong shaking or agitation at room temperature. Let stand till yellow color disappears, and repeat the addition until the yellow color is permanent for 24 hours; or if the sample is colored, until excess naphthoquinone can be detected with phenylhydrazine. Separate the addition product by distillation at room temperature in vacuum (maximum temperature 30°C.). The addition product may contain cyclopentadiene and methylcyclopentadiene dimers if large amounts of these compounds are present. Consequently it is advisable to distill soon after the first addition of α-naphthoquinone in order to obtain the later addition products free from dimers.

(b) Acyclic: Addition of maleic anhydride, as above (1% by wt.) with strong shaking until completely dissolved and let stand 24 hours. It is necessary to distill after each addition, determine the weight of diene taken up and the addition fraction is separated by crystallization. The separation of crystals from the mother liquor is best carried out (especially for very small amounts) by using Haldenwanger (Berlin) clay plates which separate very small amounts of crystals without mechanical loss of the latter.

The reaction is considered to be complete when no additional products can be found after standing 8 days.

The hydrophthalic acids present in the addition products can then be identified microchemically or by their melting points in accordance with the information given in the attached tables.

We also use maleic anhydride for removing cyclic dienes from large amounts of gasoline, after having previously determined the content with α-naphthoquinone, in order to avoid the use of large amounts of the quinone. The hydrocarbon mixture is then fractionated after removal of the dienes, and individual olefin groups in the C_5 and C_6 fractions determined. The presence of peroxides must, however, be ascertained before carrying out this fractionation, particularly in the hexene fraction, and, if present in dangerous amounts, removed by the known procedures: $Fe(CO)_5$,* heating with addition of maleic anhydride. It is often sufficient to add 10% of a high boiling hydrocarbon, for example paraffin, and distilling again. This procedure will avoid dangerous explosions. The addition of aniline can also be recommended as a high boiling liquid which can easily be removed by washing with dilute acids.

* Also $FeSO_4$

Cyclohexene and methylcyclopentene are particularly apt to form peroxides. These compounds will reform within a day after their removal. Purchased cyclohexene may contain as much as 1% peroxides and 0.01% can still be detected. These peroxides are very likely the cause of gum formation in gasolines. It is essential that peroxides be removed prior to the C_5 and C_6 olefin analyses with the V-tube, otherwise very high results will be obtained for Group I.

Addition Acids of Penta- and Hexadiene with Maleic Anhydride

			M.P. °C.
1.		Isoprene: β-methyltetrahydrophthalic acid	160
2.		Piperylene: α-methyltetrahydrophthalic acid	161
3.		2-Ethylbutadiene: β-ethyltetrahydrophthalic acid	187
4.		1-Ethylbutadiene: α-ethyltetrahydrophthalic acid	154
5.		1,2-Dimethylbutadiene: α,β-dimethyltetrahydrophthalic acid	147
6.		1,3-Dimethylbutadiene: α,γ-dimethyltetrahydrophthalic acid	162
7.		1,4-Dimethylbutadiene: α,δ-dimethyltetrahydrophthalic acid	172
8.		2,3-Dimethylbutadiene: β,γ-dimethyltetrahydrophthalic acid	178

2-8 were crystallized from ethyl acetate

The constitution of these acids was determined by dehydrogenation to phthalic acid and oxidation to benzenepolycarboxylic acids; the latter are all known.

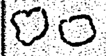
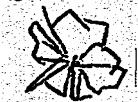
Description of Crystals

1. Thin rhombic leaflets.
2. Thick right angled plates.
3. Compact hexagonal plates.
4. Short prism of rhombic cross-section.
5. Thin dissimilar rhombic leaflets.
6. Compact tetragonal plates with a truncated corner.
7. Hexagonal plates.

The above crystal forms are typical for compounds purified by several crystallizations. It is important to have the corresponding acids prepared from pure hydrocarbons for comparison.

REACTIONS OF MALEIC ANHYDRIDE ADDITION PRODUCTS

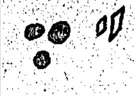
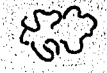
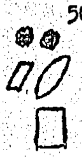
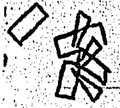
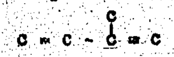
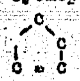
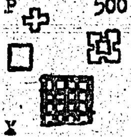
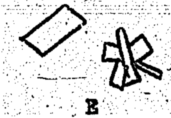
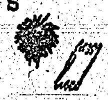
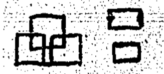
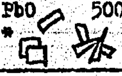
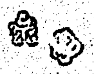
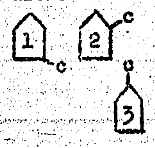
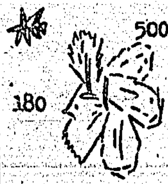
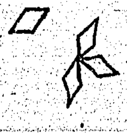
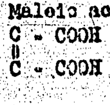
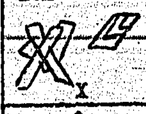
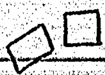
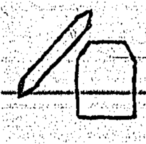
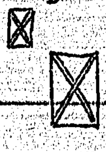
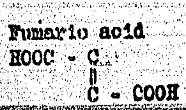
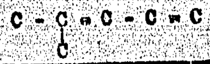
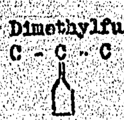
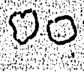
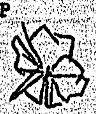
COLD, ACID, CONCENTRATED WATER SOLUTIONS

	Pb-Acetate	Cu-Acetate	Ca-Acetate	Ca-Carbonate	Sr-Carbonate	Ba-Acetate
1. Butadiene C = C - C = C	P. Cold 500  Excess Soln. Light like oxalate	P. Cold 500  * 1% Ac. Acid 	B S	B E  *	B	B
8. 1,1-Dimethylbutadiene-maleic acid C - C = C - C = C with C below second C	P cold or hot Light brown SX	P Light blue				
9. Dimethylfulvene 	P Ins. X 	P Gelatinous	P 500 	As with the acetate	500 	P 180 

P = precipitate S = soluble * = characteristic 500 = magnification B = boiling E = on evaporation X = in excess

REACTIONS OF MALEIC ANHYDRIDE ADDITION PRODUCTS

COLD, ACID, CONCENTRATED WATER SOLUTIONS

	Pb-Acetate	Cu-Acetate	Ca-Acetate	Ca-Carbonate	Sr-Carbonate	Ba-Acetate
1. Butadiene C = C - C = C	P. Cold 500  Excess Soln.	P. Cold 500  * 1% Ac. Acid	B S	B E  *	B	B
2. Piperylene C = C - C = C - C	P. 500  X	P. Flakes S 10% Acetic A.*	S	E  500		E  500
3. Isoprene  $C = C - \overset{C}{C} = C$	P 500  XS PbO → □		S	E 		
4. Cyclopentadiene 	P 500  X *	S 160  E	S * 500  high dilution	P as with the acetate	E * 	E 180 
5. 2,3-Dimethylbutadiene  $C = \underset{C}{C} - \underset{C}{C} = C$	P hot Very S in X PbO 500 * 	P Thin flakes	 500 more S than cyclo	 500 much residue E		
6. Methylcyclopentadiene 	P X very S  only with 3		P 500  *	P as with the acetate	E 500  *	
7. Cyclohexadiene Dihydrobenzene 	P *  Very insoluble X	On heating small pale green spheres with sharp edges		 500 180		500 
Maleic acid  $\begin{matrix} C - COOH \\ \Vert \\ C - COOH \end{matrix}$	Cold One drop no P then  X	Cold 500 Neutral  E	B	B  slightly S	B 	B 180 
Fumaric acid  $\begin{matrix} HOOC - C & \\ \Vert & \\ C - COOH & \end{matrix}$	P  Highly refractive in strong light like oxalate					
8. 1,1-Dimethylbutadiene-maleic acid  $C - \underset{C}{C} = C - C = C$	P cold or hot Light brown SX	P Light blue				
9. Dimethylfulvene 	P Ins. X 	P Gelatinous	P 500 	As with the acetate	500 	P 180 

P = precipitate S = soluble * = characteristic 500 = magnification B = boiling E = on evaporation X = in excess

DIOLEFIN INVESTIGATED

	Br No. - McIlhiney				Reaction with 4.5 N HBr	Treated at 0° with Neutral $KMnO_4$ in Excess
	Addition		Substitution			
	Calc.	Found	Calc.	Found		
Butadiene	592				none	not tested
Piperylene	470	450	10		polymerizes	" "
Isoprene	470	410	40		polymerizes & partly dissolves	" "
2,3-Dimethylbutadiene (1)	390					" "
3-Methylpentadiene-1,4 (1)	390	370	30		polymerizes	" "
Cyclopentadiene (1)	485	485	50		gums	" "
Sym. Methylcyclopentadiene (2)	400				"	" "
2-Methylcyclopentadiene	400				"	" "
3-Methylcyclopentadiene (2)	400				"	" "
Dihydrobenzene	400				polymerizes	" "

(1) Synthesized according to the literature.
(2) Synthesized according to new procedures.

SEPARATION AND IDENTIFICATION OF DIENES FROM CRACKED GASOLINES

The gasoline is fractionated into cuts, boiling about 20°C. apart, and each fraction stepwise treated with 1% maleic anhydride with strong agitation and 3 or 4 days' standing.

The gasoline is then distilled in vacuum at a water bath temperature, the residue treated with K_2CO_3 solution, and the latter extracted with ether. The tetrahydrophthalic acids are finally collected as an oily liquid by acidifying the K_2CO_3 solution and extraction with ether. The ether extract of the alkaline solution is kept apart since it does not contain any acids.

On strong agitation and standing for 8-14 days, about 20 to 25% of the tetrahydrophthalic acids will crystallize out from:

Crystals A, Mother liquor B

Work-up and Identification of A

Separation of the crystal mixture A by crystallization from various solvents.

The identification may be carried out:

1. By comparison with synthetic products
2. By bromine degradation to phthalic acids
3. By oxidation of the phthalic acids to the corresponding benzene carboxylic acids.

The dehydrogenation can be made with bromine, sulfur and alkaline $K_3Fe(CN)_6$; the last two have been the least used for analytical purposes.

Bromine Degradation

The customary procedure for the dehydrogenation of hydrogenated benzene compounds is that of Willstätter and Einhorn (heating with the calculated amount of Br in a sealed tube at 200°C., yield 75%) has been improved (yields 90-95%) and has been used for larger amounts.

New Method

Dissolve the anhydride in 5 times the volume of CCl_4, cool to 0°C., add Br drop by drop to saturation of the double bond. Distill off CCl_4 and heat residue to incipient boiling (HBr splitting). Add CCl_4 and excess Br. Evaporate solvent and distill residue. The unknown phthalic anhydride will crystallize immediately. When possible, identify the phthalic acid homologue or

Oxidation with $KMnO_4$, in alkaline solution to benzene carboxylic acid. Identification by means of the characteristic methyl ester.

Mother Liquor B

The greater part of the oily mother liquor can be transformed into crystalline phthalic acids by bromine dehydrogenation as above. Identification as above.

Determination of Dienes in a Cracked Distillate from Low Temperature Carbonization Tar

Fraction 60-80°C.

3297 gms. oil, from which was obtained after 4 additions: 181 g. oily addition products, or 2.3% hexadienes; 36 g. crystals or 20% of the oily addition products were separated.

Addition Number	M.P.	Wt., gms.	% of Total Crystals	Diene as Butadiene	Identification Method
1	220°	4.0	Abt. 10%	1,1-dimethyl?	Degradation and oxidation
	187	11.6	33	2-ethyl	
	147	1.0	3	1,2-dimethyl	
2	154°	12.3	54	1-ethyl	Degradation and oxidation
3	154°	4.5			
4	154°	2.0			

Determination of Dienes in a Propane Oil

4580 g. propane oil; 100 g. oily addition products or 0.8% pentadienes. Crystals separated 27.1 g., consisting of 38% isoprene-maleic acid and 62% piperylene-maleic acid addition products.

Determination of Dienes in a Cracked Gasoline Fraction 80-100° C.

12164 g. cracked gasoline; 742 g. addition products obtained from 4 additions or 2.5% hexadienes. Crystals separated 169 g. or 22.8% of the addition acids.

(data on following page)

Addition Number	M.P.	Wt., gms.	% of Total Crystals	Diene as Butadiene	Method of Identification
1	207°	0.8	0.5	Cyclic C_6H_6	
	164°	sm. amt.			
	147°	18.7	45.0	1,2-dimethyl	Crystal form & mixed M.P.
2	147°	55			
	162°	40	24.5	1,3-dimethyl	Degradation & oxidation
	174°	sm. amt.	-	?	
3	172°	15	9.0	1,4-dimethyl	Degradation & mixed M.P.
	154	23	21.0	1-ethyl	Crystal form and mixed M.P.
4	154°	10.7			

EIB/igm

Translated by E. L. Baldeschwieler
Esso Laboratories-Research Division
Standard Oil Development Company

S.O. Dev. Co. of N.J.

Translation of Technical Oil Mission Microfilm Reel #25
Pages 1434-1436
July 30, 1946
Ammonia Laboratory, Oppau

DETERMINATION OF HIGH MOLECULAR WEIGHT ALDEHYDES

It was desired to develop a procedure for the analysis of products from the Oxo reaction (aldehyde synthesis by the addition of carbon monoxide and hydrogen to olefins), whereby the aldehydes can be quantitatively determined without interference from the ketones which are generally present. The so-called carbonyl number obtained with hydroxylamine gives the sum of aldehydes + ketones.

This purpose can be accomplished by reacting the aldehyde with bisulfite with formation with oxysulfonic acids whereby only aldehydes and methyl ketones react ketones of the formula COR (where R is larger than CH) are excluded.

The bisulfite reaction has been known for a long time and is the basis for the so-called aldehyde determination according to Ripper (Monatsh. Chem. 21, 1079 (1900), also Beckurts, Massenalyse, page 9). According to this procedure, excess bisulfite solution of known strength is added to the sample and the excess bisulfite back-titrated with iodine solution. The portion of the bisulfite which acted with the aldehyde is not reduced by the iodine solution.

The Ripper procedure was first tested with low molecular weight aldehydes, but it was found also that it was satisfactory for water insoluble high molecular weight aldehydes containing more than 10 carbon atoms. After trying numerous variations, the following procedure was found to be satisfactory:

> Fifty-two grams of sodium bisulfite are dissolved in a mixture of equal volumes of water and ethyl alcohol, and the volume made up to a liter.
>
> A 1-5 gm. sample (the weight of the sample being so chosen that not more than half of the amount of bisulfite used will be combined) is weighed in a 30-ml. flask with ground glass stopper, 20 ml. bisulfite solution pipetted in. A current of CO_2 is passed for a short time to provide a blanket over the liquid. The flask is then stoppered for two hours. The contents of the flask are rapidly transferred to a titration flask, 10 ml. of a 20% aqueous solution of sodium acetate are added, and the mixture treated as rapidly as possible with N/2 iodine solution to a faint yellow coloration. The yellow coloration should be permanent for at least half a minute. A blank determination is simultaneously carried out with 20 ml. of bisulfite solution.

The results can be reported either as iodine number, i.e., iodine consumed for each 100 grams of substance, or in terms of equivalent amounts of KOH according to the customary definition of sulfite number, saponification, or carbonyl number corresponding to the aldehyde content in a one-gram sample, remembering that methyl ketone, if present, will be calculated as an aldehyde.

Since, in the determination of the carbonyl number, one mole of KOH is equivalent to one mole of ketone, but only equivalent to one-half mole of aldehyde in the determination of the aldehyde number, the latter is calculated from the following equation:

$$\text{Aldehyde Number} = \frac{(\text{Ml. } \frac{N}{2} \text{ I Soln. in Blank} - \text{Ml. } \frac{N}{2} \text{ I Soln. Consumed}) \times 14.0}{\text{No. of Gram Sample}}$$

ANALYTICAL RESULTS

The procedure was first tested with a technical dodecyl aldehyde from Agfa. The pure aldehyde was not obtained. Coal products were later obtained from Dr. Kürzinger, these products being obtained from the Oxo reaction, also fractions therefrom (S.S. Products 1-8) and finally unsaponified material obtained by the air oxidation of aldehydes, to fatty acids, and separation of the latter in the form of soaps. The fact that particularly in the latter cases the carbonyl number is higher than the aldehyde number indicates the presence of larger amounts of ketones. The carbonyl numbers were determined with methyl orange by Dr. Leithe, Laboratory Report No. 1590, also Fette and Seifen, 45, 615 (1938). The results are given in the following table.

(data on following page)

Sample	Origin	Aldehyde Number	Carbonyl Number
Dodecyl aldehyde	Agfa	220,225	227
Crude aldehyde Oxo reaction	Dr. Kürzinger	60,60	97
Crude aldehyde Oxo reaction	"	70,72	100
S.W. - Fraction I	"	127	133
S.W. - Fraction II	"	164	168
S.W. - Fraction III	"	161	173
S.W. - Fraction IV	"	136	155
S.W. - Fraction V	"	110	132
S.W. - Fraction VI	"	79	100
S.W. - Fraction VII	"	38	70
S.W. - Fraction VIII	"	23	40
U.V. 2082	"	11	27
U.V. 2116	"	9	34
U.V. 10-11	"	9	30
U.V. 8-9	"	10	34

SUMMARY

A simple titration is used for determining high molecular weight aldehydes in the presence of ketones using the bisulfite reaction.

July 30, 1946
ELB/igm

Translated by E. L. Baldeschwieler
Standard Oil Development Company

S.O. Dev. Co.
of N.J.

Technical Oil Mission Microfilm Reel #27
Pages 5 & 6, Ludwigshafen, 12/28/44
Dr. Pier Merseburg

CARBONYL AND ACETAL NUMBER

A. CARBONYL NUMBER

Weigh from 2-5 grams of sample: for substances with a very low carbonyl number use from 10-20 grams. Add 20 ml. of N/1 sodium hydroxide which is standardized daily against N/1 H_2SO_4 using bromo phenol blue as an indicator. Next add 25 ml. of 1.5 N-hydroxylamine hydrochloride solution (to which has been added 2 ml. of a 1% alcoholic solution of bromo phenol blue indicator per liter of hydroxylamine hydrochloride) and allow the mixture to stand from 1 to 1.5 hours. Then titrate back with N/1 H_2SO_4.

Calculation:

$$\frac{\text{Ml. of } H_2SO_4 - \text{Volume Consumed in Titer} \times 56.1}{\text{Weight Taken}} = \text{Carbonyl No.}$$

B. ACETAL NUMBER

A new sample is exactly acidified with 30 ml. of N/1 H_2SO_4 and to it is added as specified in (A), 25 ml. of hydroxylamine hydrochloride solution. Then heat for 1 hour on steam bath, using a reflux condenser. After cooling, add 50 ml. of N/1 NaOH. (The solution will become blue: if still yellow, repeat the experiment using a smaller sample.) After mixing with NaOH, titrate immediately thereafter with N/1 H_2SO_4 until conversion point is reached.

(Amount Consumed = Y ml.)

Blank Test

Thirty mls. of N/1 H_2SO_4 plus 25 ml. of about 1-1/2 N hydroxylamine hydrochloride solution is treated (with reflux) on a steam bath for 1 hour. After that, 50 ml. of N/1 NaOH is added and the mixture (solution) is then back-titrated with N/1 H_2SO_4.

Calculation:

$$x - y = z$$

$$\frac{z}{\text{Weight of Sample}} \times 56.1 = \text{carbonyl and acetal numbers}$$

Carbonyl number + acetal number - carbonyl number = acetal number

JBL/igm
6/5/46

Translated by J. B. Lewis
Esso Laboratories-Research Division

S.O. Dev. Co. of N.J.

Translation of Technical Oil Mission Microfilm Reel #27
Item 2, Pages 7-11

THE DETERMINATION OF CARBONYL GROUPS IN ALDEHYDES AND KETONES

Basis of Methods

1. The determination of carbonyl groups can be made through the oxime reaction employing a hot predominantly alcoholic solution containing a mixture of free hydroxylamine and hydroxylamine hydrochloride. (Stillman and Reed, C 1932, II, 2747)

2. Through the oxime reaction with an alcoholic or water solution of hydroxylamine hydrochloride at room temperature.

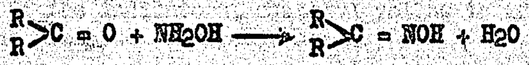
3. By argentimetric method of Ponndorf (for aldehydes only). B 64 (1931) 1913-23.

4. By special methods for estimation of carbonyl groups.

I. Oxime Reaction According to Stillman and Reed

A predominantly methyl or ethyl alcoholic solution of hydroxylamine hydrochloride is reacted with a sufficient amount of alcoholic sodium hydroxide solution to convert approximately one half of the hydrochloride to free hydroxylamine. Bromphenyl blue is then added as an indicator. The precipitated sodium chloride is filtered.

The unknown sample is dissolved in this solution and boiled under reflux.



$$\begin{matrix}R\\R\end{matrix}\!\!>C = O + NH_2OH \longrightarrow \begin{matrix}R\\R\end{matrix}\!\!>C = NOH + H_2O$$

The excess hydroxylamine is titrated with hydrochloric acid. A blank is run along with the sample and the amount of hydroxylamine reacted is determined by the difference between the two titrations.

The reaction time for aldehydes and readily reactive ketones, for example, acetone, cyclohexanone and methyl ethyl ketone is 15 to 30 minutes, while for ketones like isobutanone, benzophenone, and so forth, a reaction time of 2 to 3 hours is required.

It is recommended that for an unknown substance a variable reaction time be used.

This method is suitable for all carbonyl compounds.

Interference in the method will be caused by:

(a) strong acid compounds (dicarboxylic acids)*

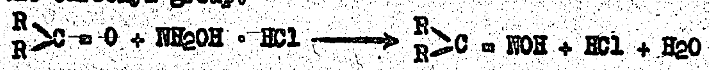
(b) aliphatic halogen substituted compounds

(c) presence of a trace of a catalytic agent (decomposition of hydroxylamine)

* In the presence of carboxylic acids, methyl orange should be used as the indicator.

II. Oxime Reaction with Hydroxylamine Hydrochloride

A predominantly alcoholic solution or for water soluble substances an aqueous solution of hydroxylamine hydrochloride is used for the determination of the carbonyl group.



$$\begin{matrix}R\\R\end{matrix}\!>C=O + NH_2OH \cdot HCl \longrightarrow \begin{matrix}R\\R\end{matrix}\!>C=NOH + HCl + H_2O$$

The HCl liberated from the oxime reaction is titrated using dimethyl yellow, bromphenol blue or methyl orange as indicator. The hydrolysis of the hydroxylamine hydrochloride is suppressed by using an alcoholic solution.

This method is applicable for most of the aldehydes (with the exception of chlorsubstituted aliphatic aldehydes) and also is suited for rapid plant control. Of the ketones only a few (for example, cyclohexanone) react to form oxime quantitatively while others (e.g. isobutanone, benzophenone) only incompletely. In the presence of such a carbonyl compound, generally distinguishable through a flash back of the color tint in the titrating solution, preference should be given to Method #1.

Of the indicators, dimethyl yellow is affected less than bromphenol blue in the presence of organic acids.

The chlorsubstituted aliphatic aldehydes give essentially too high results due to the splitting off of the chlorine.

In the presence of acetal and vinyl ether which in acid solutions are capable of dissociating into carbonyl compounds, the oxime reaction is carried out in the presence of sodium carbonate.

III. Argentometric Determination of Aldehydes (Ponndorf)

The sample is treated with silver nitrate and caustic potash solution and allowed to stand at room temperature. After acidifying the excess silver nitrate is back titrated in the usual manner. The method is applicable to aldehydes only, the ketones do not react. Formaldehyde and acetaldehyde react quantitatively, while propyl and butyl give slightly lower results. The water insoluble aldehydes (benzaldehyde, vanillin, etc.) can be determined in a boiling partially alcoholic solution. However, the presence of alcohol under certain conditions will give high results. To keep the carbonyl number in a uniform order of magnitude, the results of the argentimetric method are expressed in mg. KOH/gm. One ml. N/10 $AgNO_3$ is equivalent to 2.8 mg. KOH.

The method fails to work in chlorsubstituted aliphatic aldehydes.

IV. Special Methods for Determination of Aldehydes and Carbonyl Groups

(a) Sulfite method for formaldehyde (I.G. Analyses Nr-260).

(b) The azine method for benzaldehyde and its hydroxy-, nitro-, amino- and chlorsubstituted products. In some modifications of this method the resulting azine is weighed while in others the excess hydrazine is titrated. I.G.A. 1, 57, 127-131, 530 and 600.

(c) Phenylhydrazine method for p-aminobenzaldehyde. I.G. Analyses Nr-132.

(d) Methionic method of Vorlander - C1932, II 1552 and s.f. anal. 77, 321.

(e) Gravimetric method with 2-4-dinitrophenylhydrazine. Iddes C40, I 2834; Ind. Eng. Chem., Anal. Ed., 11 (1929) 102-103. This method gives high results on long chain aliphatic aldehydes.

PROCEDURES

I. Oxime Reaction with Hot Free Hydroxylamine (Stillman and Reed)

Reagents

1. Hydroxylamine Solution

Dissolve 40 gms. hydroxylamine hydrochloride in 30 ml. water. Dilute with 800 ml. 2B alcohol or methyl alcohol. Add with stirring 600 ml. of 0.5 N ethyl or methyl alcoholic solution of NaOH. Add 10 ml. bromphenol blue solution (see under 2) and filter.

2. Bromphenol Blue Solution

Triturate 0.1 gm. bromphenol blue with 3 ml. of 0.5 N NaOH until in solution, then dilute with 25 ml. water.

Procedure

0.01 gm. of the sample is boiled under reflux with exactly 75 ml. of hydroxylamine solution. The reaction time for aldehydes and readily reactive ketones is 15 to 30 minutes, while for the less reactive ketones (e.g. isobutanone) 2 to 3 hours are required. The solution is cooled to room temperature and titrated with 0.5 N HCl until the color changes to a greenish blue. A blank containing exactly 75 ml. of hydroxylamine and without any sample is run concurrently with the sample under identical conditions.

Calculations

$$\text{Carbonyl Number} = \frac{b}{a} \times 28.05 \text{ mg. KOH/gm. substance}$$

where a = weight of the sample in grams

b = difference in ml. of 0.5 N HCl between the blank and sample titrations

The percentage of a particular carbonyl compound of molecular weight, M, is given as:

$$\%\ \text{Carbonyl Compound} = \frac{b}{a} \times 0.05\ M$$

Amount of sample that should be taken:

Carbonyl Number Expected	Size of Sample
under 50	10 gms. (10 ml.)
50-200	3.5 " (3.5 ")
200-500	1.4 " (1.4 ")
over 500	1.0 " (1.0 ")

Comments

1. In the presence of fatty acids, methyl orange is used in place of bromphenol blue.

2. In the presence of a small amount of metal due to a catalyst, high results will be obtained due to the decomposition of the hydroxylamine.

3. Chlorsubstituted aliphatic compounds interfere in this procedure.

II(a) Oxime Reaction with Alcoholic Hydroxylamine Salt Solution

Reagent

Dissolve 350 gms. of $NH_2OH \cdot HCl$ in 1 liter of water and mix with 4 liters of n-propyl or isopropyl alcohol. Add 30 ml. dimethyl yellow (0.1% alcoholic solution) or 40 ml. bromphenol blue (0.1% alcoholic solution) as indicator. Add slowly with stirring 20% aqueous KOH until the indicator changes to yellow-orange or blue-green. By addition of a drop of 0.5 N acid to 20 ml. of this solution, the color of the indicator should change to red or greenish blue and by the addition of a drop of 0.5 N alkali to yellow or blue.

Procedure

An aliquot containing 0.02-0.03 gm. of the carbonyl compound is added to 50 ml. of the hydroxylamine hydrochloride solution, stoppered and set aside for 30 minutes. The more difficultly soluble samples can be dissolved beforehand in n- or isopropyl alcohol. In the presence of carbonyl groups, the color of the indicator changes to red (dimethyl yellow) or yellow (bromphenol blue). A blank containing 50 ml. hydroxylamine and 10 ml. water is run concurrently with the sample. After standing for 30 minutes the sample is titrated with N alkali until the color of the sample matches exactly that of the blank.

Calculation

$$\text{Carbonyl Number} = \frac{b}{a} \times 56.1 \text{ mg. KOH/gm. sample}$$

where a = weight of sample in gms.
b = ml. N alkali required.

Amount of sample that should be taken:

Carbonyl Number Expected	Size of Sample
under 50	about 10 gms. (10 ml.)
50-100	" 5 " (5 ")
over 100	" 2 " (2 ")

Comments

1. A flash back of the indicator color to red or yellow after the end point has been reached signifies the presence of a slow reacting carbonyl compound. Method #1 should be used.

2. In determining the carbonyl number on mixtures containing fatty acids, dimethyl yellow should be used as indicator.

3. High results are obtained on chlorsubstituted aliphatic aldehydes.

II(b) Oxime Reaction with Aqueous Hydroxylamine Salt Solution (Only for Water Soluble Substances)

Procedure

An aliquot containing 0.02-0.03 gm. of the carbonyl compound is added to 50 ml. 1 N hydroxylamine hydrochloride or sulfate (69.5 gms. $NH_2OH \cdot HCl$ or 82 gms. $(NH_2OH)_2\ H_2SO_4$ per liter) and 100 ml. water, stoppered and set aside for 30 minutes. After standing for 30 minutes, the sample is titrated with 1 N alkali using as an indicator either methyl orange or bromphenol blue.

The slight acidity contained in the hydroxylamine salt solution is titrated with 1 N alkali solution to the same end point using the same indicator as on the sample on a blank consisting of 50 ml. of the hydroxylamine salt solution diluted with 100 ml. water. The blank is run concurrently with the sample.

Calculations

$$\text{Carbonyl Number} = \frac{b}{a} \times 56.1 \text{ mg. KOH/gm.}$$

where a = weight of sample in grams.
b = difference in ml. of 1 N alkali between the titration of the sample and the blank.

The percentage of a particular carbonyl compound is calculated from its molecular weight, M, as follows:

$$\%\ \text{Carbonyl Compound} = \frac{b}{a} \times 0.1\ M$$

III. Oxime Reaction with Free Hydroxylamine at Room Temperature

This method is used when besides the carbonyl group to be determined there is present a substance which in acid solutions is capable of dissociating into a carbonyl compound, e.g., acetal or vinyl ether. The sample is dissolved in neutral n-propanol or neutral acetone-free isopropanol.

An aliquot corresponding to 0.02-0.03 gm. of the carbonyl group is added to a mixture of about 60 ml. of 1 N hydroxylamine salt solution and exactly 50 ml. of 1 N NaOH and 50 ml. water. The flask is stoppered and set aside or shaken. The solution is titrated with 1 N acid using methyl orange or bromphenol blue as indicator. A blank is run in a similar manner using a mixture of approximately 60 ml. of 1 N hydroxylamine salt solution and 50 ml. of water.

Calculation

$$\text{Carbonyl Number} = \frac{b}{a} \times 56.1 \text{ mg. KOH/gm.}$$

where a = weight of sample in grams.
b = difference in ml. of 1 N acid between the blank and sample titrations.

The percentage of a particular carbonyl compound is calculated from its molecular weight, M, as follows:

$$\%\ \text{Carbonyl Compound} = \frac{b}{a} \times 0.1\ M$$

IV. Argentimetric Determination of Aldehydes (Ponndorf)

Into a 100-ml. volumetric flask add in succession 25 ml. of 0.1 N $AgNO_3$, 0.5 ml. 1 N $MgSO_4$ and 10 ml. of the sample containing at most 1 millemole of aldehyde. Add with adequate mixing 15 ml. of 0.2 N sodium hydroxide and shake the reaction mixture vigorously for 5 minutes. After further addition of 6 ml. of 0.2 N alkali, shake the flask again for 5 minutes. Now add with adequate mixing 5 ml. of 1 N KOH within 30 seconds and shake for 2 minutes. Then add in small portions 5 ml. of 20% sulfuric acid. Dilute the mixture to the mark and filter through a dry filter paper. Reject the first 20 ml. of the filtrate. Titrate 50 ml. of the remaining filtrate with 0.1 N ammonium thiocyanate in the usual manner using ferric alum as an indicator.

Calculations

$$\text{Carbonyl Number} = \frac{b}{a} \times 2.8 \text{ mg. KOH/gm.}$$

where a = weight of sample in grams.
b = ml. of 0.1 N $AgNO_3$ used.

This method gives quantitative results with formaldehyde and acetaldehyde while for higher aldehydes low results are obtained. It is recommended in these cases to lengthen the reaction time and to heat the solution to boiling. Water insoluble substances are dissolved in methanol.

High results are obtained on chlorsubstituted aliphatic aldehydes.

JH/igm

Translated by J. Holowchak
July 1, 1946

THE TEXAS COMPANY

PORT ARTHUR RESEARCH LABORATORY

TECHNICAL OIL MISSION
REEL NO. 27, ITEM NO. 56
BAG 2169, TARGET 30/4.03

DRYING AND DRY-KEEPING THROUGH THE USE OF SILICA GEL

Gasbelangen 6, 133-38 (1939?) #10

DRYING AND DRY-KEEPING THROUGH THE USE OF SILICA GEL

by

A. Adam

Introduction

In the present manufacture of materials and products drying as well as the dry-keeping plays an outstanding role. There are many processes in the course of which water (or other liquids) is used as an expedient. In most cases the liquid has to be removed after the completion of the process. This form of drying is encountered in various industries. The removal of water after washing and drying processes and the removal of the volatile oils which are used in the manufacture of lacquers and varnishes are examples.

Various soil and chemical products have to be dried before they can be shipped or stored to avoid spoiling or deterioration. It would be laborious to enumerate all the procedures of the technique which fall under the head of drying.

Drying in General

The most common method of drying is to extract the water from a solid material by evaporation. Therein one has to differentiate between materials with hygroscopic properties and those without. If a non-hygroscopic material is in unsaturated air (or any other gas), i.e. in a surrounding which is capable of taking up more water vapor than it already contains, then the water contained in the material will evaporate. The time required for the evaporation depends on the temperature and the relative humidity of the surrounding. (Here follows a definition of relative humidity and evaporation temperature and a discussion about the influence of the temperature, the air velocity, and the hygroscopic character of the drying speed. Remark of the translator.)

For most industrial purposes a speedy drying process is desirable. Besides an acceleration of the air velocity around the material to be dried, the drying can also be speeded up by increasing the temperature of the air current, thereby reducing the relative humidity simultaneously. The more hygroscopic the material to be dried, the higher the temperature required.

<u>Fig. 1.</u>

Diagram of a silica gel dryer with one absorber.

<u>Fig. 2.</u>

Diagram of a silica gel dryer with two absorbers.

In this well-known drying method, in which air heaters and ventilators form a part of the drying apparatus, gas-air-heaters have already found extensive application.

There are, however, various processes in which an increase of the air temperature is undesirable in the interest of the product. One way to achieve faster drying without raising the temperature consists in pre-drying the air, that is, in reducing the relative humidity while maintaining the temperature. There, two drying processes are connected in sequence: first the air is dried and then the material is dried with dried air.

The air can be dried by bringing it into contact with a strongly hygroscopic material which is capable of extracting large volumes of water vapor from the air and by doing so reducing its relative humidity. Water may also be removed from the air by cooling through condensation.

Dry-Keeping

Until now only the drying of a material has been discussed; but the dry-keeping is of no less importance especially where hygroscopic materials are concerned. Most products have to be stored for shorter or longer periods of times and, of course, this must not impair their quality.

As we have already mentioned, hygroscopic materials take up moisture from their surroundings as the relative humidity increases. For most hygroscopic material there exists an upper limit above which a further increase of moisture content means deterioration or possible deterioration of the quality. In order to avoid this the relative humidity of the storage space has to be kept below a certain value. This again can be achieved by two methods, (1) by raising the temperature of the storage space to a degree at which the relative humidity remains below a certain value; (2) the water vapor content of the air in the storage space can be reduced so that the permissable relative humidity is not overstepped. The first method requires heating, the second, drying and dry-keeping of the air.

The difference between the two methods consists in the fact that by raising the temperature of the storage space heat is continuously lost through the walls which naturally is not the case when the second method is used. Here the water vapor which penetrates into the storage space has to be dealt with, and, eventually, has to be removed. Through efficient construction and insulation, penetration can be kept at a minimum, and this is less expensive than the heating method. This difference is especially noticeable when a material requires a low relative humidity and therefore a higher temperature if the heating method is applied.

As was the case with drying, here too one might have to deal with materials which, cannot be exposed to raised temperatures, therefore excluding the heating method. There are, obviously, various reasons for preferring the dry-keeping of storage spaces and the drying of the air to the heating of the storage spaces. The air may be dried for this purpose by the same method previously discussed.

Fig. 3.

Air dryer for the deacidification building and pump chamber of the water works of Apeldoorn. (the gas-mixture air-heater is in the foreground.)

Fig. 4.

Silica gel drying unit.

Silica Gel

How important a role the drying may play in the drying of materials as well as in the dry-keeping of storage spaces etc. evolves clearly from the preceding discussions. Among the various hygroscopic materials which come under consideration for the drying of air the product known under the trade name Silica Gel has already found wide applications. This product has two properties which are important for this purpose: it is capable of absorbing a major part of its own weight in water at a relative humidity below 100%, and it is capable of reactivation after it has been saturated with water. By the latter is meant that the water may be expelled by heating and that the product can thus be reused for the drying of air. The efficiency does not suffer by the reactivation.

The silica gel used in the air drying units consists of hard, glass-like grains which remind one of quartz. It is a product obtained by a special method from a soluble silicate and sulfuric acid, whereby it attains this special consistency which makes it suitable for the purpose mentioned.

In regard to the structure, one has to visualize that the product consists of thin-walled channels which cannot be seen even with the strongest microscope. The volume of the pores occupies 50-70% of the total volume of the product and the inner surface is in excess of 280 m^2/cm^3 of silica gel. Normal silica gel can absorb 50% of its own weight of water from saturated air. In doing so it does not change its volume and does not give the impression of being moist ("absorption").

The Silica-Gel Drying Unit

To dry air, silica gel grains are spread on a perforated plate in an absorber and air is sucked or blown through it. As long as the saturation point of the silica gel is not overstepped the air comes out completely dry. At a certain saturation of the silica gel it is useless to continue the drying process and it is necessary to reactivate the gel. This is done by sucking or blowing a stream of air heated to 150° C. through the gel bed until the water content of the gel is again down to about 5% of its dry weight. After this a new drying period may be commenced.

Whether it is possible to stop the drying of the air during the reactivation period or whether it is necessary to connect a second adsorber depends on the drying project. Fig. 1 and 2 are flow-schemes for silica gel drying units with one or two adsorbers respectively. From Fig. 1 can be seen that the ventilator, at the given position of the valves, leads the air through the chamber to be dried and through the adsorber. This is the drying period. If the valves are turned, the outside air is sucked in, heated by the air-heater, sucked through the gel bed and then expelled together with the water taken from the bed. This is the activating period.

Fig. 2 shows that the right adsorber serves for drying while the left one is being reactivated. By turning the valves the reverse takes place.

Fig. 3 is an example of a small unit with two adsorbers (the photos for Fig. 2-7 were put at our disposal by the N.V. Droogtechniek en Luchtbehandeling in Rotterdam); in the upper flat box the adsorbers are situated. The air-heater for the gas-mixture can be seen in the foreground; at the left is the ventilator which is used for activating; the valves are beneath the adsorbers. This installation keeps the relative humidity in the deacidifying building at a low point, and in the pump chamber it avoids the condensation of water on the relatively cold pipe lines and pumps during the summer. From this it can be seen that these drying units serve purposes other than that of keeping stored goods dry.

Fig. 4 is a picture of the drying unit of the N.V. Mekog, seen from above. Here the two large rectangular adsorbers can be seen, which alternatingly perform the drying. Between them are the four switch valves, which have been shown in Fig. 2. At the left of the adsorber, further back, the gas air-heater, which is constructed as a heat exchanger, can be seen. This construction deviates from the one given in Fig. 2 inasmuch as the air to be dried is sucked in from outside. This stream of air, about 7500 m^3/hr., after drying is blown into the drying chamber of 50,000 m^3 volume. This creates a slight pressure in the chamber and the excess air escapes through special openings and incidental leaks. This chamber stores artificial fertilizers which are strongly hygroscopic and which deteriorate when they gain in moisture. The relative humidity in this room has to be kept below 28%.

These two units are so constructed that they work completely automatically, which is usual for this kind of dryer.

The drying has to be done only when the air in the drying chamber becomes moist. By the means of a humidity regulator (humidostat) the drying ventilator is turned on and off as necessary. When, by some method or other, it becomes apparent that one of the adsorbers is saturated, the valves can be switched automatically and the reactivation begun. As soon as the gel bed is completely dry the activating period is terminated. This is usually done with a thermostat.

The Air Heater

It is important for the gas industry that illuminating gas has proved to be a suitable fuel for the air heaters. The automatic running of a gas-air-heater is a simple and safe matter. Another advantage is the complete combustion of the gas without the formation of soot. Therefore, it is possible to mix the combustion products of the gas directly with activating air in such a ratio that the desired temperature, 150° C., is obtained. It has been determined that the combustion products of the gas have no unfavorable influence on the gel; however, the absence of soot is a necessary condition. A gas-air-heater of this kind, a so-called gas-air mixture heater, is not only much cheaper to purchase than a heat exchanger in which the combustion gases are separated by walls from the air to be heated, but it is also more economical in its use because practically all the heat in the gas serves for the heating of the gel.

The gas-air mixture heater has already been pointed out in Fig. 3. This one has a capacity of 4 m^3/hr. of gas. The unit of N.V. Mekog shown in Fig. 4 has, for special reasons, a gas-air-heater in the form of a heat exchanger of 60 m^3/hr. of gas; this is shown in Fig. 5. There is also a gas-air mixture heater, used as a reserve, with the same capacity.

Several Other Plants Which Use Illuminating Gas

The oldest plant of this kind which uses illuminating gas for the dry keeping of warehouses in which artificial fertilizers are stored is in the Staatsmijnen. Their plant differs in principle only slightly from the one of N.V. Mekog. The gas air heater here works according to the mixture system.

Fig. 5.

Photo of the gas air heater of the
drying plant of N.V. Mekog in Velsen.

A more recent plant is the one of N.V. Het Nederlandsche Veem in Rotterdam. The floor of the warehouse which is shown in Fig. 6 contains a room of 55,000 m^3 for the storing of about 10,000 tons of crude sugar. To avoid spoilage the relative humidity of the room must not exceed 58%. For this purpose there is a silica gel unit which is capable of blowing 10,000 m^3/hr. of dried air into the storage room. The adsorbers are able to extract more than 100 kg./hr. of water from the air which has to be dried. The activation is carried out by an automatically working unit with a gas-air mixture heater of 90 m^3/hr. of gas. Fig. 7 presents a picture of it. The regulating and safety devices can be seen in the foreground.

Fig. 6.

Warehouse "San Francisco" of HAL. used by N. V. Nederlandsche Veem in Rotterdam.

Fig. 7.

Gas-air mixture heater of the silica gel unit of N.V. Mekog.

Naturally there are many more applications for this drying method than the ones mentioned above because the number of objects and products which have to be protected from moisture during storage is very large. Besides food and chemical products one could think of furniture, furs, paper (archives), etc.

The danger of condensation has only been mentioned incidentally. This danger occurs especially during the summer in rooms which cool down during the night or which remain cool through their position, such as cellars. Machines and electrical equipment can suffer much damage through condensation. The drying of the air would in most cases offer a solution to the problem.

Translated by: Johanna Carl (Independent Translator)
Edited by: V. H. Kane (Chem. Eng., TTCo.)
Joyce Day (Res. Lib., TTCo.)

THE TEXAS COMPANY

PORT ARTHUR RESEARCH LABORATORY

TECHNICAL OIL MISSION
REEL NO. 27, ITEM NO. 57
BAG 2169, TARGET 30/4.03

LIQUID-DRYING EXPERIMENTS WITH SILICA GEL

Nitrogen Division
Lo/Op. 299 December 19, 1938

LIQUID-DRYING EXPERIMENTS WITH SILICA GEL

The drying of water-containing organic liquids with silica gel has been attempted. For this drying silica gel B, large pored and in grains of 2 - 4 mm, was used.

Two series of experiments were conducted: (1) 250 cm^3 of liquid were led through a silica gel layer 50 cm. high; and (2) 250 cm^3 of liquid were shaken with silica gel. In both cases the same amount of silica gel B, 80 g., was used.

The water content of the liquids was determined before and after the drying. In the case of these liquids which are infinitely miscible with water (alcohol, acetone) this was done by specific gravity; in the case of the liquids which have a limited miscibility with water (ether and higher alcohols), and in the case of those which take up only slight amounts of water (benzene, gasoline etc.), it was determined by the calcium hydride method. This method is based on the fact that the calcium hydride reacts with water to form the hydroxide according to the equation:

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$$

The amount of hydroxide formed is measured and from it the water taken up is calculated according to the above equation. These determinations are done with a special apparatus built for us for this purpose; the values obtained are very accurate. The results of the drying experiments are given in the following tables:

Liquid	Drying by passing through 50 cm layer of silica gel: Water content before	after	degree of dryness obtained	Drying by shaking up with silica gel: Water content before	after	degree of dryness obtained	Method of water determination
ethyl alcohol	10%	10%		10%	10%		sp. gr.
	5%	5%		5%	5%		" "
	2%	2%		2%	2%		" "
methyl alcohol	10%	10%		10%	10%		" "
	5%	5%		5%	5%		" "
	2%	2%		2%	2%		" "
acetone	10%	10%		10%	10%		" "
	5%	5%		5%	5%		" "
	2%	2%		2%	2%		" "
ethyl ether	4.307%	0.64%	86%	4.307%	0.65%	85.9%	CaH_2-Method
	2.081%	0.57%	72.6%	2.081%	0.56%	73.2%	" "
isobutyl-	3.265%	0.73%	77.6%	3.265%	0.76%	76.8%	" "
alcohol	1.471%	0.43%	70.8%	1.471%	0.41%	72.2%	" "
benzene	0.21%	0.014%	93.2%	0.21%	0.011%	94.8%	" "
	H_2O partial. suspended			H_2O partial. suspended			
	0.085%	0.012%	85.9%	0.085%	0.011%	87%	" "
	H_2O dissolved			H_2O dissolved			
carbon-	0.164%	0.009%	94.5%	0.164%	0.011%	93.3%	" "
disulfide	0.014%	0.005%	64%	0.014%	0.007%	50%	" "
gasoline	0.047%	0.010%	78.7%	0.047%	0.009%	80.8%	" "

No final conclusions were reached on determining how much the silica gel can be charged. In order to charge 80 g. of silica gel with 10 g. of H_2O, approximately 14 litres of water-saturated benzene (approximately 0.085%) would have to pass through the silica gel. Moreover, until now no method has been found to determine with approximate accuracy the water absorbed by the silica gel. The xylene method shall be tried next because the expulsion of the water by heating and subsequent condensation was not successful. By measuring the water of condensation from a benzene charge, 18 - 31 g. H_2O/ 100 g. of silica gel has been found by reactivation of the latter. However, these results fluctuated and could not be reproduced.

SUMMARY

The dehydration experiments of organic liquids by the means of silica gel above gave the following results:

1. Alcohols and acetone, infinitely miscible with water, are not dried with silica gel.
2. Higher alcohols (isobutyl alcohol) and ether, which are miscible with water to a limited extent, were partially dehydrated.
3. The organic liquids which take up only slight amounts of water (benzene, gasoline, carbon disulfide) are practically completely dried. The silica gel absorbed the dissolved as well as the suspended water. The liquids contain only about 0.01% H_2O after drying.

Translated by: Johanna Carl (Independent Translator)

Edited by: V. H. Kane (Chem. Eng., TTCo.)
Joyce Day (Res. Lib., TTCo.)

Standard Oil Company (Indiana)

INFORMATION DIVISION TRANSLATION T47-21

API-TOM Reel 36, Frames 111-113 (Item 2)

1) Polymerization:

Preparation of highly knock-resistant naphtha from the light olefines (particularly propylene and butylene) of gasol by the process of polymerization.

This results from the combination of smaller, related molecules to form larger hydrocarbon molecules. The work is done mainly with catalysts containing phosphoric acid.

Product: Polyner naphtha, a mixture of iso-olefines, iso-paraffins and cyclic hydrocarbons in the naphtha-region with properties valuable for engines.

Procedure: By the Ruhrbenzene U.O.P. Procedure (Universal Oil Products)

2) Aromatization:

Conversion of the heavy naphtha fractions (80°-200°C) to aromatic hydrocarbons, i.e. to derivatives of benzene and its homologs. There are two possible procedures: One either can separate one fraction at a time and obtain the pure aromatic compounds with high yields, or else the total fraction is charged, and thus up to 50% of aromatic hydrocarbon is formed in one pass.

Product: a) pure aromatic hydrocarbons (toluene)
b) knock-resistant naphtha with high aromatic content.

Procedure: A procedure developed by the Ruhrchemie Aktiengesellschaft at their experimental plant.

3) Dehydration: Formation of olefines from saturated hydrocarbons of gasol. The olefines obtained are then available for polymerization and further chemical treatment.

Products: Propylene and butylene.

Procedure: Not used at Ruhrchemie Aktiengesellschaft and Ruhrbenzine. Is now being worked on in the laboratory.

4) Isomerization: Formation of branched hydrocarbon groups from straight-chain hydrocarbons or transfer of the double bond within the hydrocarbons.

Products: Mixture of branched hydrocarbons (iso-heptane, iso-octane, etc.)

Procedure: Not used at Ruhrchemie Aktiengesellschaft and Ruhrbenzine. Is now being worked on in the laboratory.

5) Catalytic Cracking: Cracking of higher-molecular n-paraffin-hydrocarbons somewhat below the usual cracking temperature with certain large-surface catalysts, with formation of low-boiling naphtha-like hydrocarbons of largely isoparaffin and isoolefin structure.

Products: Highly valuable and highly knock-resistant naphthas.

Procedure: Own procedure of Ruhrbenzine is under construction.

6) Thermal Cracking: Cracking by heat. Cracking of higher hydrocarbons without the use of catalysts. (e.g. for the obtaining of starting materials for our lubricating oil plant)

Products: Mixtures of naphtha-like hydrocarbons with high olefin content. Cracked naphtha.

Procedure: In the lubricating-oil plant, Dubbs-process. In the naphtha improvement: T.V.P.-plant. (True vapor phase)

7) Distillation: Transformation of a mixture of hydrocarbons through heating into hydrocarbon vapors, with subsequent condensation of these vapors. According to the boiling behavior, so called fractions can be separated immediately. This method is of the greatest importance in the laboratory technique and the large-scale manufacture of a variety of industries. The main task of the distillation is, on the other hand, purification of the distillate, i.e. the distilled liquid, on the other obtaining or separation of liquid products with exactly determined boiling points or boiling point regions.

8) Refining: Purification:
Removal of harmful materials from hydrocarbon mixtures through treatment with lye and acids, distillative solvents, fuller's earth, etc.

Products: Purified naphthas, purified oils, purified cracked naphthas, etc.

Procedure: At Ruhrbenzin a fuller's earth process for purification cracked naphtha is being developed. In our lubricating-oil factory, the purification of the oils is accomplished by a Tonsil*-treatment developed here.

(*TR: Acid-treated clay)

9) **Stabilization:** Transformation of a naphtha to a storable condition. In case of the Fischer-synthesis a simultaneous removal of naphtha vapors from crude gasol and of gasol residues from crude naphtha by a type of pressure distillation.

Products: Gasol-free storable naphtha.
Naphtha-free gasol.

Translated by E. Rothstein, March 5, 1947
Checked by C.C.M. March 6, 1947
Requested by R. F. Marschner
Information Division Translation 747-21

"Polymerisation"
Ruhrchemie Aktiengesellschaft
Oberhausen-Holten
May 9, 1941
3 pages, no illustration

Standard Oil Company (Indiana)

INFORMATION DIVISION TRANSLATION T47-22

API-TOM Reel 36, Frames 497-502, Item 31
To Professor Martin, et. al.
Preparation of R_4- and R_5-Aviation Gasolines for Berlin.

Duplicated on Reel 46, Item 49, Frames 909 - 914

The closely-cut C_4- and C_5-fraction from the catalytic cracking, which had undergone a polymerization, was used as starting material. In this case the C_4 fraction should be as free of C_3 as possible, since even small amounts of propylene greatly reduce the superchargability of the polymerization product. With the C_4-fraction it was possible to use a 90% polymerization, since the various degrees of polymerization do not affect the superchargability as greatly. With the C_5-fraction only a 60% polymerization was carried out, since an increase of the yield seemed to bring about a depression of the superchargability curves. However, upon repetition of these experiments no difference in superchargability was shown between 60 and 70% polymerization. Therefore the clarification of this point is still being worked on. The poly-products formed were subsequently distilled, namely the C_4-product up to 165°, the C_5 product from 60-165°.

These fractions were completely hydrogenated and treated with 0.005% by weight "Stabisol" (I.G.-Inhibitor.) They were sent to Berlin without the addition of lead tetraethyl, namely as:

R_4 : C_4 - polymer,
R_5 : C_5 - polymer,
R_{4+5} : Mixture R_{4+5} (1:1).

R_4-Product: The gas used had the following composition:

Composition:	Vol %	Wt. %
$n-C_4H_{10}$ $i-C_4H_{10}$	9.1	9.7
$1-C_4H_8$ $2-C_4H_8$	51.9	51.6
$i-C_4H_8$	39.0	38.7
	90.9 Total Olefin	90.5 Total Olefin

According to this, of the total butylene 90.9% approximately 43% was isobutylene.

The polymerization was carried out at the technical testing station (IF) at 60 atm. abs., 130-140°C, and a load of 1:1 by weight.

The exhaust gas gave the following picture:

	Vol.%	Wt. %
n - C_4H_{10} i - C_4H_{10}	55.7	58.1
C_2H_4	1.4	0.7
1 - C_4H_8 2 - C_4H_8	41.5	40.5
N_2	1.4	0.9

This means that by gas analysis the polymerisation amounted to 82% by volume as well as by weight, and that the isobutylene was completely worked up. Calculation of the experiment shows good agreement:

Input: 750 l. x 0.6 = 450 kg. x 90.3% = 406 kg. olefin
Poly-naphtha: 495 l. x 0.733 = 363 kg. olefin

This means that 89.5% of the olefin was transformed to naphtha.

According to the precision distillation of the impure product 86% come over up to 165°; according to the re-run distillation, from 475 l. input, 405 l. of product boiling up to 165° were obtained, which equals a distillation yield of 85%. Therefore, the yield of R_4, relative to the total input, is 90.3% olefin x 89.5% polymerization yield x 85% distillation yield = approximately 69%.

On graph I is shown the distillation curve of the R_4-poly-impure product. Table I shows a collection of the most important properties of the hydrated product, cut at 165°.

R_5-Product: The C_5-fraction used had the following composition:

n- i- C_4H_{10}		1.1	1.0
1- 2- C_4H_8		8.9	7.0
i - C_4H_8	89.3%	2.6	2.0
i - C_5H_{10}	total	36.8	90.0
n - C_5H_{10}	olefin	41.0	
n - C_5H_{12}		9.6	

Thus of the total pentenes, 47% are isopentylenes.

The polymerization was carried out at 60 atm. abs., 110°C and a load of 1:1.2 by weight. The impure poly-naphtha obtained also underwent a precision distillation (graph I), during which the deep-condensation product and the C_5 fraction were analyzed simultaneously. The precision analysis shows that 27 vol. % = 23.6% by wt. of deep-condensation product and 27.6 vol. % = 26.0% by wt. of C_5-fraction are contained in the impure product. This mixture looks like this:

			Vol. %	Wt. %
n- i-	C_4H_{10}		1.5	1.1
1- 2-	C_4H_8		7.5	6.0
i-	C_4H_8	73.5% residual olefin	0.5	0.4
i-	C_5H_{10}		18.6	86.8
n-	C_5H_{12}		20.5	
n-	C_5H_{10}		46.9	
t-	C_6		4.7	5.7

Purely by volume, this would equal a 67% C_5-polymerization, while by weight it amounts to only 60%, as shown by the following calculation: After the polymerisation the fraction boiling up to 51° = 23.6 wt.% of deep-condensation product and 26 wt. % C_5 = 49.6%

This mixture contains 5.7 wt. % C_6 = 2.8%

Therefore, up to 51°, really 46.8% come over, which means that 53.2 wt. % must have been polymerized. Calculated in terms of the olefins, this equals a 60% polymerisation. Since 43.8 wt. % boil from 51°-165°C according to the precision distillation, the distillation yield is 82%. Thus the yield of R_5, relative to the total input, equals: 90% olefin x 60% polymerisation x 82% distillation yield = appr. 44%.

The re-run distillation yield gives the following picture:

Input	960 L	Vol %	670 kg.	Wt. %
-50°	434 l	45.3	272 kg.	40.5
50°-165°	375 l	39	285 kg.	42.5
over 165°	31 l	3.2	24.2 kg.	3.6
loss	120 l	12.5	88.8 kg.	13.2

The unaccounted-for loss would have to be looked for mainly in the fractions below 50° and above 165°, according to the precision analysis. On graph I is shown the boiling point curve of the C_5-impure product, and on table I the properties of the hydrogenated and distilled product.

R_{4+5} Product: As previously mentioned, this material consists of a mixture of R_4 and R_5 in the volume ratio of 1:1. The physical and chemical data on this mixture are also found in table I.

As can be seen from the table, the 3 naphthas completely satisfy all necessary conditions. Through the lesser polymerisation of the C_5-fraction, the R_5-greatly resembles the R_4-product in regard to its motor octane number as well as its superchargability, the degree of which is reproduced in graph IV.

/S/ Spiske

TABLE I

Properties:	R_4	R_5	R_{4+5}
d_{20}	0.7129	0.7059	0.7095
nD_{20}	1.4016	1.4018	1.4016
Reid	0.12	0.45	0.29
Iodine No.	0.0	0.0	0.0
Neutralisation No.	0.0	0.0	0.0
Blow-away test (Gum Residue?)	1.0mg/100 cm^3	0.8mg/100cm^3	0.8
Bomb Test (100°, 240 min. Ind.)	1.0mg/100 cm^3	1.0mg/100cm^3	1.0
Bomb Test (200°, 240 min. Ind.) 1.2 Pb+Stabisol	5.8mg/100 cm^3	7.2mg/100cm^3	6.0
Start of boiling	76°	35°	60°
End of boiling	173°	167°	169°
T° 10%	104°	49°	79°
T° 50%	114°	129°	120°
T° 95%	150°	156°	164°
% Loss	2.0	6.5	4.0
% Distillate	97.0	93.5	95.0
% Residue	1.0	1.0	1.0
S.K.Z. *	114.9	119.	116.1
motor octane number	92.4	90.8	91.9
motor octane number + 1.2 Pb	103.7	100.5	102.8

TR: *Boiling Characterization No. ?

Translated by E. Rothstein, March 3, 1947
Checked by C.C.M. March 6, 1947
Requested by R. F. Marschner
Information Division Translation T47-22

"Herstellung des R_4-und R_5-Flugkraftstoffes für Berlin"
Ruhrchemie Aktiengesellschaft
Oberhausen-Holten
June 15, 1942
4 pages, 2 graphs

Attachments on Original

Figure I

Precision distillation analyses of crude poly products R_4 and R_5.

Volume per cent versus Temp. °C.

Figure II Supercharge curves for El-100, R_4, R_5 and R_4+R_5, kg/cm ^{2} versus air excess numbers.

S.O. Dev. Co. of N.J.

Translation of Technical Oil Mission Microfilm Reel #38
Foot 28 - Frame 9
Foot 29 - Frame 1

ANALYTICAL METHODS FOR A SYNTHESIS PLANT

Page No.	Method No.	Method
454	59	Test for the activity of catalysts for the ammonia syntheses according to Casale
476	60	Determination of isobutylene in gas oils by the addition of hydrochloric acid (compare analytical method #54)
485	61	Determination of hydrocarbons from one to five carbon atoms and the isomers of butane and butylene by fractional distillation

ELB/igm

Translated by E. L. Baldeschwieler
Standard Oil Development Company

Standard Oil Company (Indiana)

INFORMATION DIVISION TRANSLATION T47-7

API-TOM Reel 40, part of Item 11, Frames 24-50
Ruhrchemie A.G. Oberhausen-Holten, March 29, 1939
To: Professor Martin, Dr. Hagemann, Dir. Alberts
"Catalytic Polymerization of Unsaturated Hydrocarbons"

The submitted work treats a polymerization process, by which the so-called solid phosphoric acid catalyst of Ipatieff was employed. For a better view of the total material this is divided into 3 summarized single groups, and so

A) Polymerization of condensate naphtha
B) Polymerization of gasol (Trans.: L.P.G.)
C) Polymerization of condensate naphtha + gasol
  1) without C_2H_4 addition
  2) with C_2H_4 addition

Goal of the Method - Preparation of liquid, knock-resistant hydrocarbons, which lie within the boiling limits of motor fuels, starting out from a low-boiling fraction of condensate naphtha or gaseous olefins on the other hand. The inclusion of the condensate naphtha gives the possibility of transformation of these low-boiling light bodies into high boiling heavy naphtha of equal or higher octane number and with it an improvement of the specific gravity of the "F.T." (Trans.: Fischer-Tropsch?) product.

Before the subdivision in groups in the further discussion of the work, the common characteristics of the three groups of the procedure is to be anticipated here. These are:

1) The apparatus - It consists of two iron tubes each 1000 mm. long with an interior diameter of 22 mm. which are connected with one another by a strong capillary. At the beginning and end of the reaction tube is found a Hofer valve for the purpose of regulation of the addition and withdrawal of the reaction charge at constant pressure. Each tube possesses an electric heater with two measuring places for the temperature of the external jacket. On account of the small diameter, it was not possible to accomplish inner temperature measurements by means of built-in thermal elements. The heating length of the furnace amounted to ca. 1700 mm. so that the reaction space amounted to about 650 cc. The furnace was filled with a catalyst (ca. 600-700 g.).

2) Execution of the process - Out of a bomb with submerged tube the charge to be polymerized is forced into the apparatus by means of N_2 and streamed through both slightly inclined furnaces. At the end of the second furnace the released polymerized product flows through a condenser into a measuring receiver. It possesses a reflux cooler, and is closed in order to be able to measure the non-condensable products as gas.

3) Catalyst - A polymerization catalyst specified by Ipatieff was employed. It had the following composition:

60 g.	magnesium chloride
50 g.	magnesium oxide
100 g.	kieselguhr
50 g.	starch
20 g.	alumina
800 g.	phosphoric acid 82%

The specified amount corresponds to about one-half liter of catalyst.

4) Conditions of the experiment - Only the temperature was kept constant at 200°C for the main experiments since this proved to be the optimum for our furnaces after several test experiments. Pressure and residence duration (Trans: contact time) were greatly varied, as will be shown.

5) Method - As motor fuel only the polymers lying within the boiling limit of 200°C are important. The problem in the far-reaching working up of the olefins was as much as possible not to allow liquid polymer to go beyond the dimerization. There was introduced therein as a criterion of the strength and quality of the polymerization a ratio (k=polymerization ratio) which shows how many volume percent of the constituents boiling over 200° correspond to the volume percent of the polymerized constituents at 70°C.

For example, a condensate naphtha boiling up to 70°C is polymerized. The boiling curve of the polymer shows at 70° 40 vol.% and at 200°C 90 vol.% distillate. In this case:

$$K = \frac{10}{60} = 1:6$$

i.e. that in a polymerization of 60 mol. % at 70°C, 10% boils over 200°C. The numerator of a good polymerization should be as small as possible, the denominator as large as possible.

A. Polymerization Condensate Naphtha

For feeling out of the whole range, a series of preliminary experiments were carried out in a standing furnace with an interior width of 50 mm. and a length of 2500 mm., which contained 1700 g. of catalyst. The pressure was varied between 1 at. - 10 atm. the temperature between 150°-250°C and the velocity of the charge between 250 cc - 800 cc. condensate/hr. It is shown that a raising of the temperature or the pressure or a lowering of the charge rate increases the polymerization. However, in the same degree the amount of the portion boiling above 200°C also increases, so that in all experiments in the first furnace the average polymerization ratio was 1:4, immaterial if the polymerization was high or low. So, for example, experiment 17 at 200°C, 3 atm. and 400 cc. condensate/hr. shows a $K = \frac{10.5}{45} = 1:4.2$ while experiment 19/I at 200°C, 1.5 atm. and 800 cc had a $K = \frac{5}{21.5} = 1:4.3$. The polymerization in experiment 17 was twice as large as in experiment 19/I, while the polymerization ratio in both was practically equal.

A condensate naphtha which had the following constants was used in these preliminary tests:

Boiling initial = 25°C
Boiling end point = 76°C
Specific gravity = 0.6470
Index of refraction = 1.3782
Vapor pressure = 1.4 at @38°C
Olefins = 84%

One obtained from it crude polynaphtha which according to the vigor of the polymerization had changed the constants, for example, as follows:

Crude Prod.	Weakly Poly.Prod.	Vigorously Poly.Prod.
Specific gravity	0.660	0.715
Refractive index	1.392	1.416
Vapor pressure	1.2	0.8
Olefins	64%	46%
Boiling point initial	25°C	32°C
Boiling point end point	25°C	320°C

The fractional distillation of this product from 20 to 20°C (Trans: obvious error in the text. Probably 20°-70°C) showed an almost proportional increase of the olefin refractive index and specific gravity curves.

The analysis of the true polymer product (portion boiling between 80-200°C) yielded the following data:

d_{20} = 0.7452	d_{20} = 0.7430
nd_{20} = 1.4255	nd_{20} = 1.4246
olefins = 78%	olefin = 81%
OZ = 94.5%	OZ = 94%

(Trans :OZ = octane number

Since the polymerization ratio of the experiments in a new furnace of 20 mm. inside diameter was more favorable immediately at the start, the further experiments were carried out only in the furnace of 20 mm. i.d. described above.

For the first series of experiments condensate naphtha boiling to 80°C was introduced into the new furnace. Also here the rise of the portion boiling over 200° by vigorous polymerization can be observed, as the following Table I indicates in the lowering of the polymerization ratio.

Table I

	Conditions			Volume %		K - Polymerization
Exp.	Temp.	Press.	Speed cc/hr.	Polym.	over 200°C	Ratio
16/1	200°	1 at.	250	7	-	0:7
16/2	"	2 at.	"	13.5	1.5	1:9
16/3	"	4 at.	"	17	2	1:8.5
16/4	"	10 at.	"	31	8	1:4.0

For all that, the polymerization in all experiments was small; the polymerization ratio, on the other hand, significantly better than in the first furnace.

For the second series of experiments a 20-70° boiling fraction of a previous polymerization (5 at. 200°C, 400 cc. K = 1:5) was utilized as the charge. Thereupon an interesting observation was made. While in the other polymerizations up to 10 atm. the polymerization ratio remained almost constant here it becomes ever better on utilization of higher pressures. As the supplement I shows the boiling curves intersect between 100-180° in order to rise steeper and more rapidly at higher pressure. The following Table II renders the rise of the polymerization ratio well.

Table II

	Conditions			Volume %		K - Polymerization
Exp.	Temp.	Press.	Speed cc/hr.	Polym.	over 200°C	ratio
20/1	200°	4 at.	250	22	3	1:73
20/2	"	10 at.	"	42	6	1:7.0
20/3	"	20 at.	"	43.5	4.5	1:9.7
20/4	"	50 at.	"	48	4	1:12
20/5	"	100 at.	"	41	2.5	1:16.4

One sees here in spite of a vigorous polymerization an improvement of the polymerization ratio which is striking at high pressure as experiment 20/5 shows. This has its basis thereon that on use of 100 at. pressure, the polymerization of light naphtha at 200°C no longer exists in the gaseous but completely in the liquid phase. The application of still higher pressure - we have gone up to 150 atm. - showed itself as aimless, as was to be foreseen.

API-TOM Reel 40, Frames 24-56

Continuation of "Polymerization of Unsaturated Hydrocarbons"

The application of high pressure was also used now in the polymerization of condensate naphtha. It was to establish a much greater polymerization and indeed at increasing pressure of 10 atm. to 100 atm. 31 volume % polymer to 58 vol.% whereupon the polymerization ratio increased from 1:4 to 1:6.5. In spite of doubled polymerization, the volume % of components boiling above 200°C rose only from 8% up to 8.5 volume %. The red curve in supplement II again yields a good polymerization ratio. One sees from it that at establishing greater polymerization (at 10 atm.) it rises steeply, in order to remain afterwards almost equal in spite of increase of the polymerization.

A further advantage of the high pressure was the greater amount of charge and connected with it the greater amount of condensate per hour which one can obtain at equal contact time. With a greater charge rate goes hand in hand a further employment of the polymerization ratio. Therewith, the characteristics for the further course of the work were given:

1. higher pressure
2. greater amount of charge

Since good results were realized in the second series of experiments with a fraction of the pre-polymer, a condensate naphtha treated in the cold with "Tonsil" (Trans: a certain acid-treated clay) was introduced. We believed, namely, that by the pre-polymerization the gum and resin-forming materials would be dissolved out and wished to reach this same effect by the treatment with "Tonsil" in the cold. This was not realized. The polymerization ratio was not improved and the boiling end point even pushed out yet to 270°. (Table III, graphically: supplement II). Also an olefin-poor mixed charge -obtained from 3 parts condensate naphtha and one part pre-polymer fraction of 20°-70°- showed no change in the polymerization ratio. (Table III, graphically: supplement II).

From the attached Table III, is to be seen that also by application of high pressures a change of the temperature or the speed of the charge causes a shift of the polymerization, without markedly changing the polymerization ratio. This becomes only more favorable by introduction of pre-polymerized products. After proof of influence of temperature, pressure and speed in the one-step polymerization we came by means of this knowledge to the two-step.

At first we carried out the two-step polymerization so that we introduced the condensate naphtha weakly polymerized and the fraction 20-70° of the pre-polymer (ca. 90%) into the same reaction furnace as in the main polymerization under mild conditions (150°, 1 atm. 1000cc) for the main polymerization. It is shown, thereby, that a two-step polymerization and indeed weak pre-polymerization with strong main polymerization showed better results only at greater charge rate (2000 cc/hr), while the simple polymerization at a speed of 1000 cc/hr cuts off somewhat better. The supplement V graphically presents the ratio of the two-step polymerization in comparison with the one-step polymerization.

A second method which can be claimed as a pre-polymerization was the treatment of the condensate naphtha with "Granusil" in the vapor phase. For this and the light naphtha was allowed to flow through a superheater into the reaction tube proper which was filled with "Granusil". The throughput occurred at a temperature of 225° and a speed of ca. 2000 cc/hr.

Since thereby naphtha was obtained, which had the boiling end point of 198-220°, no loss resulted in relation to motor fuel. In the starting of the furnace one obtains a small weight difference between the entering charge and the end product which continually became smaller (decreasing C-separation) and completely discontinued after several liters of naphtha throughput, so that also in this relationship, no noteworthy losses occurred since no gas cleavage occurred. The constants of the products before and after the treatment were:

Initial boiling		38°C	Initial boiling		38°C
End boiling		73°C	End boiling		198°C
Gas loss		8.5%	Gas loss		5.5%
d_{20}	=	0.6602	d_{20}	=	0.6723
nd_{20}	=	1.3871	nd_{20}	=	1.3911
olefins	=	80%	olefins	=	77%

The product treated previously was distilled to 70° (it shows a boiling curve up to ca. 200° whereby ca. 85% went over up to 70°) and the distillate introduced to the main polymerization. There was then obtained an average polymerization ratio of 1:10.5 (graphic supplement III.) As supplement V shows the ratio at best to lay in this combination, "Granusil" treatment as weak pre-polymerization with following strong phosphoric acid polymerization.

On the other hand, if the pre-polymer (boiling end point 204°) after the "Granusil" treatment is not distilled to 70°, but directly introduced into the main polymerization, so falls the polymerization ratio--also by application of different charge rates--again to average 1:6 (graphic representation: supplement IV).

Even an increase of the speed to 4500 cc/hr, the maximum which our apparatus could reach, yielded in weak polymerization the formation of products which boiled over 200°C. It must, therefore, be accepted that in the naphtha charge are materials which come together to higher polymers with much greater speed than the normal polymerization occurs. Therefore, it is not possible also in strong polymerization to keep the boiling end point accurately at 200°C. In the experiments with the two-step process with Granusil we obtained products with boiling end points which lay between 210-220°, accordingly can be utilized practically as a motor fuel.

B. Polymerization of Gasol (L.P.G.)

For carrying out this experiment, the same reaction furnaces, as previously mentioned, were taken, and the influence of temperature, pressure and speed of charge were systematically investigated. The numerical compilation of the characterized experiments are shown in Table IV. The essential observations, which are yielded from it, should be singly counted.

The Gasol charge contained 60% $C_3H_6 + C_4H_8$ and 4.5% C_2H_4.

Change of Speed at 100 at. and 10 at.

In the first series of experiments of the table, the rate of the charge/hr. was varied at equal temperature (200°C) and equal pressure (100 at.). One recognizes very distinctly the proportionate decrease of the $C_3 + C_4$ polymerization with increasing amount of condensate/hr. while in the C_2H_4 polymerization between 500 and 1000 cc polymer/hour large irregular decrease takes place.

At low pressure (10 at.) the rate change is connected with a great decrease in the total polymerization. The rate of 600 cc condensate/hr. utilized in experiment 47/III was the largest which could be reached at this pressure.

Change of the Pressure at 250 cc and 1000 cc Condensate/hr.

An increase of the pressure at lower rate is followed by a uniformly rising polymerization of the $C_3 + C_4$ olefins, while the irregular increase of the polymerization of C_2H_4 here lies between 10 and 50 atm.

One sees from the compilation certain parallels between the two groups: change of rate and change of pressure. As example follow the data of 2 polymer-naphthas (crude product) obtained from gas oil:

	weakly polymerized (48/II)	strongly polymerized (44/I)
sp. gravity	= 0.7165	0.7433
refractive index	= 1.4164	1.4273
olefins	= 79%	70%
boiling point Initial	= 23°	35°
boiling point End	= 252°	261°
gas loss	= 7%	6%
50% point	= 107°	137°
until 200°C	= 91 vol.%	87%

The octane number of all polymeric naphthas from gasol lies between 96-98 according to the research method.

C. Polymerization of Condensate Naphtha and Gasol

1) Without addition of C_2H_4

A mixture proportion of 1:1 was prepared in the bomb. The gasol analysis yielded: $C_3H_6 + C_4H_8 = 43\%$. As brought forth from Table V, one finds again exactly the same products as in the polymerization of gasol alone. So, for example, the equal decrease of the C_3+C_4 polymerization by the increase of the charged amount at 100 atm., of the rapid decrease by the change of rate at low pressure etc. Also no essential displacement of 200° point is to be noted by introduction of this mixture. It lies, for example, in a strong polymerization (92% olefin working up) at 86 vol.% while at a weaker polymerization (23% working up of the olefin) it rises to 93 vol.%. One also sees here the most favorable results by application of high pressure combined with greater amount of charge.

2) With addition of C_2H_4

Since in the mixture of gasol and condensate naphtha, the C_2H_4-content was so low, that one could not exactly measure the course of the C_2H_4 polymerization, a three-way mixture was prepared for clarification of this question which appeared important for the direct treatment of cracked gases in the "Poly-plant" during conservation of the ethylene on the one hand and for the clarification of the question of the possibility of the complete co-polymerization of the ethylene on the other hand. The gas mixture had the following olefin composition: $C_3H_6 + C_4H_8 = 42.1\%$ and $C_2H_4 = 22.2\%$.

Table VI shows the series of experiments with increasing pressure and increased amount of charge. The polymerization of the C_3+C_4 olefins proceeds in the known ways while the polymerization of C_2H_5 is significantly less, but also grows with increasing C_3 polymerization. At low pressures 5-10 atm., it is practically zero in order to reach to 18% at a 90% C_3+C_4 polymerization.

Table VII shows the result of the investigation of three poly-naphthas from gasol and gasol plus condensate naphtha in different proportions.

From Table IX is to be learned the knock resistance of different naphthas.

Table X shows several residual gas analyses of the polymerization of condensate naphtha and gasol, and gasol alone.

Table VIII renders the properties of several naphthas cut to 200°C and the higher poly-products.

Experiences with the phosphoric acid catalyst

Essentially for its effectiveness and long stability is the form in which the phosphoric acid exists. The correct choice of dehydration is decisive therefor. We have found on optimum at 250°. In one experiment the temperature was allowed to rise to 310°. The effectiveness of the catalyst decreased rapidly.

Several experiments by additions of small amounts of water (0.5-1% of the throughput) in order to retain activity for a longer time were wrecked after a short time by the limited diameter of 20 mm. of our oven by obstruction of the passage with stuck-together catalyst. For this purpose it was necessary to lead in direct steam or send the water through a superheater. These experiments, which lead to very good results, will be treated in the following work regarding polymerization.

Since we did not allow the reaction furnace to run continuously, it was flushed with nitrogen at somewhat elevated temperature, about 230°C each day at the end of the experiment in order to free it entirely of charge. It is possible that this process at the same time represents a kind of regeneration of the catalyst, because we already have the last catalyst in use the fourth week with an operating hour number of 142, without its effectiveness diminishing.

Summary:

The polymerization of olefins with solid phosphoric acid catalyst is a process patented by U.O.P. The application of high pressure shows better results, according to our investigations, since polymerization in the liquid phase strongly represses over-polymerization. A further advantage is the increase of the amount of charge. Recently this process of high pressure polymerization which was independently found by us, was applied on a large scale by U.O.P.

Explanation for the several supplements

Supplement I, III and IV render the boiling curves of the polymer products obtained from condensate naphtha and the polymerization ratio obtained at 70°C.

Supplement VI shows the boiling position of the poly-products from the mixture of condensate naphtha and gasol in the proportion of 1:1 with the corresponding polymerization ratio and the value of the C_3-C_4 polymerization.

Supplement VII illustrates the boiling curves of the gasol poly-product with gas analysis and C_3-C_4 working up in vol.%.

Supplement II presents the polymerization ratio (vol.% over 200°C: vol.% polymerization at 70°C) as a function of pressure, temperature and amount of charge by differently-treated condensate naphthas. Here it is very clear (on the red line) to recognize the advantage of the application of high pressure to polymerization. While at point P_1 (200°; 10 at. 250 cc) the 8 vol.% of constituents boiling over 200° coming out at 31° vol.%. polymerization rises in point P_2 (200°C, 100 at. 250 cc) in spite of a polymerization increase to 55%, to only 8.5 vol.% of the portion boiling over 200°C. i.e. at a total increase of the polymerization of ca. 44%, it comes to only a 6% (6% of 8%) increase of the constituents boiling over 200°.

Supplement V shows the polymerization ratio in relation to pressure charge and temperature of several condensate naphthas in one step and two step polymerization process. One sees that the two step polymerization cuts off best (red line) with a "Granusil" pre-polymerization. In a 47% polymerization the constituents boiling over 200° amount to only 4.5% in this case and increase to 8 vol.%. in a 63% polymerization (i.e. a complete working up, since there were no more olefins in the condensate naphtha).

Information Content of the Tables

Table
III - Single step condensation of condensate-naphtha
IV - Gasol polymerization
V - Polymerization of condensate naphtha and gasol without C_2H_4
VI - Polymerization of condensate naphtha and gasol with C_2H_4
VII - Properties of several poly-naphthas boiling to 200°
IX - Octane number data of several poly-naphthas
X - Residual gas analyses.

Table III

Completion of several experiments of the single step polymerization carried out at different temperatures, pressure and charge.

		Conditions			Vol. %		Ratio
Exp.	Charge	Temp. °C	Pressure(at)	Cond.cc/hr	Polym.	over 200°	K
23/III	Condensate naphtha	150	100	1000	39	6.5	1:6
23/III	"	150	100	250	51	8.5	1:6
23/II	"	200	100	1000	52.5	8.5	1:6.2
23/I	"	200	100	250	55	8.5	1:6.5
28/II	"	200	130	3000	55	8.5	1:6.5
28/III	"	250	130	3000	65	10	1:6.5
28/IX	"	250	130	4500	59.5	9	1:6.6
26/I	Condensate Naphtha treated Cold with Tonsil	200	100	250	62	10	1:6.2
26/II		200	100	1000	55.5	8.5	1:6.5
26/III		250	100	1000	84	14	1:6.0
25/I	Condensate naphtha 3 parts and fract. 20-70° Of a pre-polymer	200	100	250	50.5	9	1:5.6
25/II		200	100	1000	10.5	7	1:5.8
25/III		150	100	1000	30.5	5	1:6.1

Table IV

Compilation of several experiments of gasol polymerisation.

Gasol: 60% $C_3H_6 + C_4H_8$, 4.5% C_2H_4

Exp.	Conditions Temp.	 Pressure	 cc/hr	Polymerization of $C_3H_6 + C_4H_8$	Polymerization of C_2H_4	Remarks
44/I	200	100	250	90%	61%	
44/II	200	100	500	84%	48%	
44/III	200	100	1000	70%	16%	Change of rate at 100 atm.
48/I	200	100	1000	70%	16%	
48/III	200	100	1500	63%	missing	
48/II	200	100	2000	56%	14%	
47/I	200	5	250	73%	12%	
47/II	200	10	250	80%	13%	Change of pressure at 250 cc
47/III	200	10	600	39%	0%	
47/IV	200	50	250	92%	66%	
47/V	200	50	1000	46%	0%	Change of pressure at 1000 cc
47/VI	200	100	1000	71%	17%	
47/II	200	10	250	80%	13%	Change of rate at 10 atm.
47/III	200	10	600	39%	0%	

Tables V and VI

Polymerisation of Condensate Naphtha and gasol

1) Without addition of C_2H_4

Gasol = $C_3H_6 + C_4H_8 = 43\%$ $C_2H_4 = 0.5\%$

Exp.	Conditions Temp.	 Pressure	 cc/hr	Polymerization of $C_3H_6 + C_4H_8$	Polymerization of C_2H_4	Remarks
49/V	200	100	250	92.5%	Because of the small amount of 0.5%, exact measurements not possible.	
49/VIII	200	100	500	82%		
49/VI	200	100	1000	65%		
49/VII	200	100	2000	23%		
49/II	200	10	1000	5.8%		

2) With addition of C_2H_4

Gasol: $C_3H_6 + C_4H_8 = 42.1\%$ $C_2H_4 = 22.2\%$

52/I	200	5	150	50%	0%
52/II	200	10	250	55%	1%
52/III	200	50	250	89%	14%
52/IV	200	50	500	72%	11.5%
52/V	200	50	1000	51%	5.3%
52/VI	200	100	250	90.5%	18.0%
52/VII	200	100	500	80%	14%

Table VII

Investigation of 3 poly-naphthas:

G = poly naphtha from gasol, refined over "Granusil", distilled to 165°C.

G_1= poly naphtha from gasol and condensate-naphtha (1:1) mixture of fraction 20-70° and 70-200°C in the ratio of 1:1, refined over Granusil, distilled to 165°C

G_2= poly naphtha as G_1 only the mixture ratio of the fractions 1:2

Designation	G	G_1	G_2
D_{20}	0.6871	0.6967	0.7040
ND_{20}	1.4106	1.4052	1.4082
Reid pressure	0.68/38°	0.47	0.49
Olefins(Kattw.)	77%	67%	57%
Iodine Number	253.5	227.2	229.0
*Octane Number	Test motor in repair		
*Resin-test	205.5mg/100cc	15.5	25.5
Boiling-initial	36°	38°	40°
Boiling end	157°	178°	176°
Gas loss	3%	3%	3%
50% Point	81°C	89°	98°
95% Point	132°C	160	157°

Engler Analysis			
Vol.%	G	G_1	G_2
5	48	52	56
10	52	56	62
20	58	65	91
30	67	72	78
40	74	79	87
50	81	89	98
60	89	102	109
70	99	121	126
80	112	137	137
90	127	152	152
95	146	157	156

* Octane Number: motor method

* Resin test: Bomb test method, original + 0.02g cresol/100 cc

Ind. Time min. G = 180, G_1 = 250, G_2 = 240

Table VIII

Properties of several naphthas - cut to 200°C

Conditions of Experiment	5 at.200°C 400 cc/hr.	5 at.195°C 250 cc/hr.	100 at.,200°C 250 cc/hr.	100 at. 200°C 500 cc/hr.
Charge	Condensate naphtha	Condensate naphtha and gas oil	Condensate naphtha	Gasol
d_{20}	0.6886	0.6997	0.7278	0.729
nd_{20}	1.4006	1.4048	1.4230	1.4190
Reid pressure 30°C	0.95	0.88	——	——
Olefins %	72%	66%	57%	72%
Octane number	94	89	90	96.5