Hendrick Conical Tumbler Blenders FOR SOLID-SOLID MIXING

Hendrick Conical Tumbler Blenders were developed for the rapid and efficient mixing of solids in all states of particle division ranging from large pebble to 200 mesh size powders. These Tumbler Blenders are available in a wide range of sizes and capacities, from laboratory models to large units for the blending of five tons of solids per batch. Conical Tumbler Blenders are ideally suited to the blending of:

- Pigments or colors.
- Plastic moulding powders.
- Ores for assay purposes.
- Salts in pharmaceutical preparations.
- Dyestuffs.

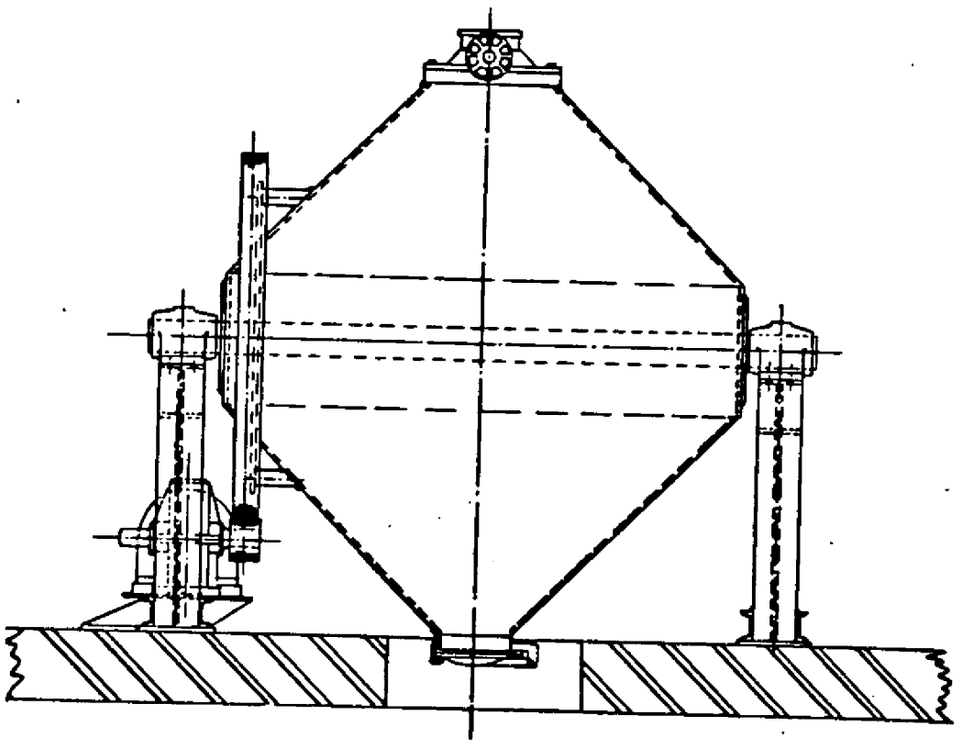


Fig. 12. Hendrick Conical Tumbler Blender; 10,000 pound capacity; built for the blending of plastic moulding powders.

Hendrick Conical Tumblers owe their efficiency to two important features:

1. End-to-end tossing action.
2. Scattering lattices.

The end-to-end, or bin-to-bin, tossing action is developed by setting the angular velocity of the tumbler at that point at which the centripetal and centrifugal forces acting upon any particle in the bin are critically equal. This tossing action prevents the rolling of the mass on itself, thus guaranteeing a maximum rearrangement of spacial relationships between particles per spin of the tumbler. The exclusive Hendrick "baffled-fall" feature is obtained by the positioning of a lattice or grating so as to exert a scattering action on the tumbled mass. These lattices or gratings may be incorporated in removable sections. They prevent the unhampered falling of the mass in large aggregates.

The Hendrick Conical Tumbler Blender consists of two conical bins attached by girth welds to a cylindrical belt. Either separate trunnion members emanating from the cylindrical belt, or a through-shaft passing through the entire Tumbler (depending on the construction preferred) are used to support the tumbler. The trunnions or through-shaft are housed in rigid pillow blocks. The motivation of the drum may be effected through a direct coupling of a trunnion with the output shaft of a motor-reducer drive, or a motor-reducer and pinion and spur gear assembly.

Drives for Hendrick Conical Tumbler Blenders are designed for "inching" of the tumbler into position for charging or discharging.

The compactness of the Hendrick Conical Tumbler plus its extraordinary efficiency as a Blender gives it the following advantages:

Low floor space requirement per unit capacity.

Rapid, time-saving blending.

Low blending costs.

Hendrick Barrel and Tube Blenders

Hendrick Barrel and Tube Blenders are suited to those instances of solids blending in which a grinding or comminuting action is essential. Like the Hendrick Conical Tumbler Blenders, the Barrel or Tube Blenders are available in a large range of sizes and capacities.

The Barrel or Tube Blenders are frequently provided with internal baffles which induce a longitudinal exchange of materials in the Barrel or Tube in addition to the local action caused by grinding balls or bars.

The basic mass motion in the Tube or Barrel Blender is an end-over-end or "kneading" action.

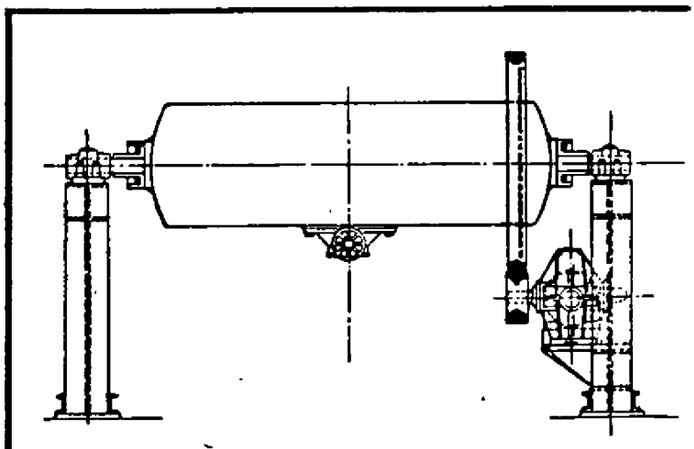


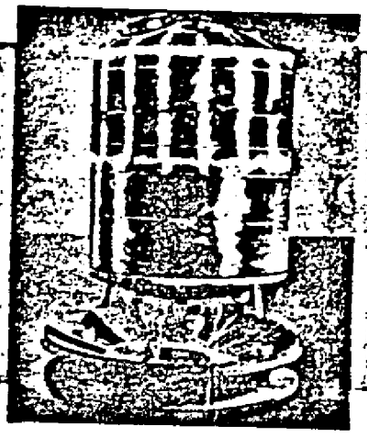
Fig. 13. Hendrick Barrel and Tube Blender; 5,000 pound capacity.

ADDITIONAL HENDRICK PROCESS EQUIPMENT

In addition to the Mixing Equipment described in the foregoing pages, the Hendrick Manufacturing Company builds:

- Resin Kettles
- Autoclaves
- Nitrators
- Sulphonators
- Emulsification Equipment
- Oil Blowing Vessels
- Chlorinators
- Paint Thinning Vessels
- Reactors
- Blending Equipment
- Cotton Thinning Equipment
- Complete Pilot Plants
- Complete Commercial Production Plants
- General Welded Pressure Vessels
- Special Process Equipment

All the above equipment is available in all ferrous as well as non-ferrous metals and alloys, and in the clad-steels. Hendrick Processing Equipment equipped with Hendrick Mixing Units offers uniform high quality construction, easy assembly, and maximum processing efficiency.



For further information concerning the mixing equipment described in this bulletin, or for engineering assistance in the solution of mixing problems or the design and construction of chemical process equipment, please address:

HENDRICK MANUFACTURING COMPANY

Process Equipment Division
CARBONDALE, PA.

Also Manufacturers of Perforated Metals, Mitco Open Steel Flooring, Mitco Shur-site Treads, and Mitco Armorgrids for the process and other industries.

6/6/50

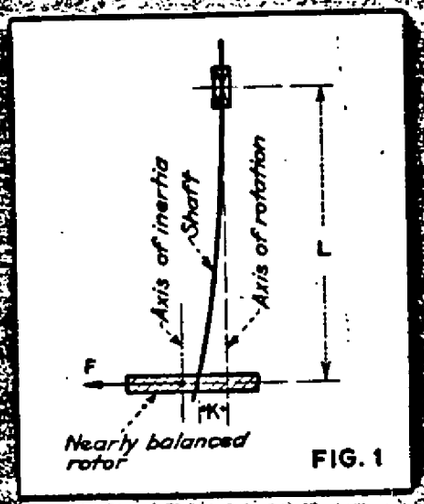


Fig. 1. Free end shaft with nearly balanced rotor.

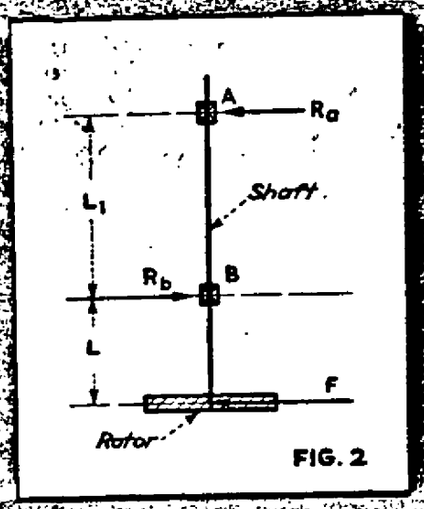


Fig. 2. Rotor shaft guided by bearings above rotor.

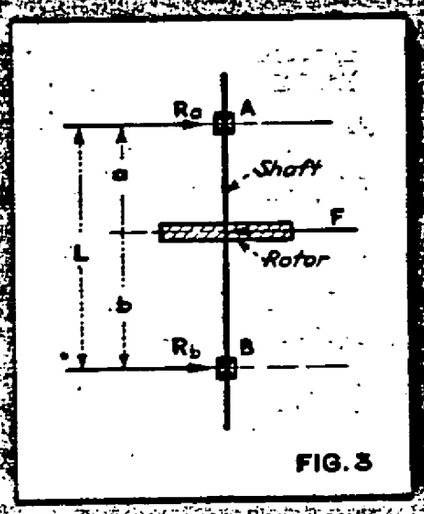
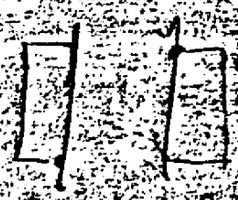


Fig. 3. Rotor shaft guided by bearings above and below rotor.



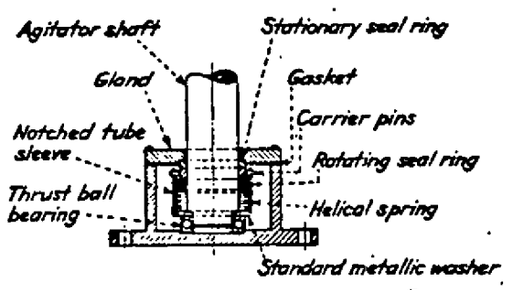


FIG. 4

Fig. 4. Thrust bearing assembly for submerged service.

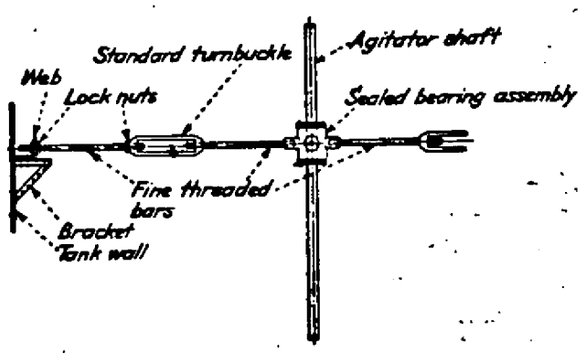


FIG 5

Fig. 5. Method of supporting bearing assembly with tie-rods.

Precise Fractionation Assembly

overed by United States Patent No. 2,387,479.

Features

1. Fractionation efficiency up to 50 theoretical plates.
2. Fractionation charges from 2 ml. to 5000 ml., inclusive.
3. Temperature range from room temperature to 752°F. (400°C).
4. New precision device for adiabatic temperature control.
5. Atmospheric or vacuum fractionations.
6. Three interchangeable fractionating columns.
7. Improved spiral packing for small column.
8. Rapid fractionation with complete visability.
9. Easily operated with a minimum of experience.
10. Special machined supports for assembling apparatus.
11. Precision control panel for operating the column's "Staggered Dual Heating Unit" and still pot.
12. Special aluminum alloy pot heater with low temperature lag.
13. All metal parts non-corrosive to normal laboratory atmosphere.
14. Rapidly assembled or dismantled.

An efficient and versatile laboratory fractionation column assembly with a new method of adiabatic temperature control for complete fractionation of many types of organic liquid mixtures either at atmospheric pressure or under vacuum.

For additional experimental results, methods of operation, and details, see article, "Efficient and Versatile Laboratory Fractionation Column Assembly," by F. Todd, *Ind. Eng. Chem., Anal. Ed., Vol. 17, page 175, 1945.*

Write for article reprint and TECHNICAL BULLETIN 100 for more detailed information.

Precise Fractionation Assembly

The following parts are described in TECHNICAL BULLETIN 100:

PRICE LIST

G 17950	FRACTIONATION COLUMN ASSEMBLY	$175.
G 17955	CONTROL PANEL	75.
G 17960	ALL PURPOSE LABORATORY HEATER	25.

ACCESSORIES

(not included in the above assembly price)

G 17965 STILL POTS, Pyrex glass, with 19/38 standard taper joint, thermometer well, set of eight assorted sizes with the following capacities: 10, 25, 50, 100, 250, 500, 1000, and 2000 ml. ..... Set **$37.**

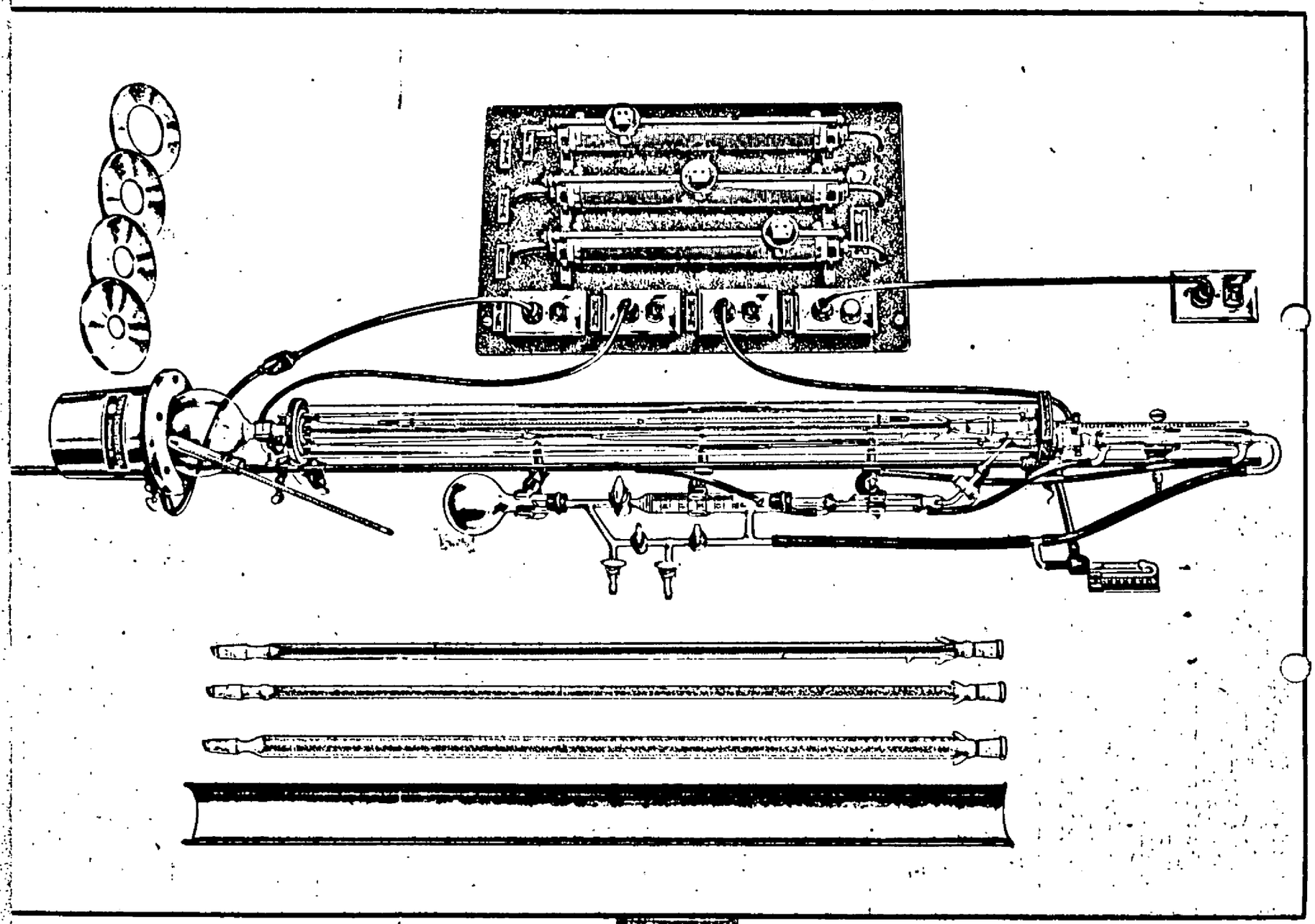
G 17970 VACUUM RECEIVER, Pyrex glass, 50 ml. capacity, graduated in 1 ml. divisions, with five (5) standard taper stopcocks for making necessary connections..... **$25.**

G 17975 HELICES, Pyrex glass, 3/32" dia. for packing both the 12 and 25 mm. columns..... Lot **$27.**

(These helices are non-corrodible and are a generally useful size for the majority of atmospheric or vacuum precise fractionations. The precision spiral Monel packing is normally included for the 5 mm. vacuum jacketed column.)

Distributed by

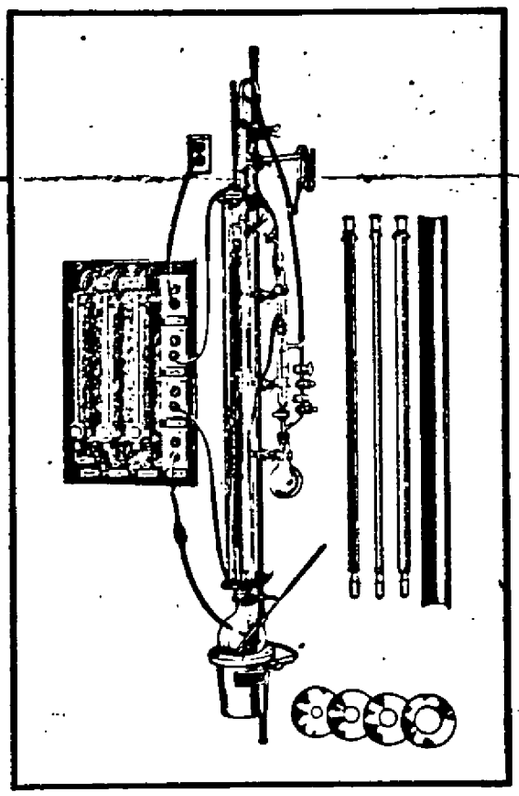
The EMIL GREINER Co.



Precise Fractionation Assembly

USED BY THE NATIONAL BUREAU OF STANDARDS

88 Vanice
60 manifold
25 3 cfg.
25 packing
10 jacket
15 still head
10 assembly
25 ft tank
248



THIS PRECISE FRACTIONATION ASSEMBLY is the the result of a comprehensive and critical study of practically all significant reports on methods and apparatus for precise laboratory fractionations which were published in the United States, British, French, and German scientific literature. In addition, the methods and apparatus surveyed have been subjected to exhaustive experimental tests in our laboratories. These tests have shown the need for a versatile and efficient fractionation apparatus of more practical design to meet the varied fractionation requirements arising in chemical laboratories. To meet this need, a new, truly versatile and highly efficient laboratory fractionation column assembly was developed with several practical features which enable this single assembly to eliminate the use of a number of fractionation units for solving different problems.

The use of the recommended packings in the three interchangeable columns of this new assembly gives unusually high fractionation efficiencies over comparatively wide rates of boiling either at atmospheric pressure or under vacuum. These particular packings eliminate the frequent disadvantages of the use of precise reflux ratio control devices which are invariably bulky, tedious to operate, and frequently have large hold-up capacity.

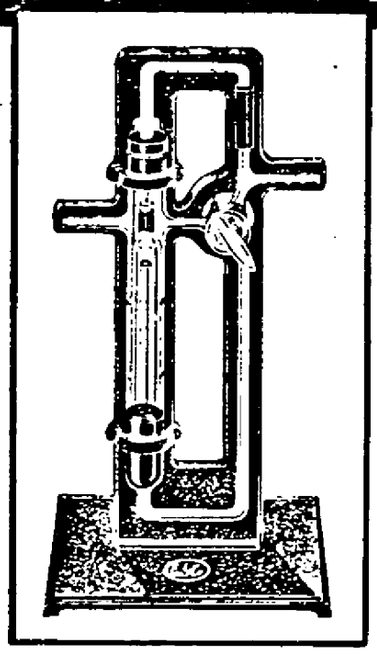
Among other features, the still head of this assembly overcomes the above disadvantages by having a special compact design, constant operation, very low hold-up capacity in operation (0.6 ml.), and ease of control. The compact design allows the entire still head to be completely enclosed within the heater jacket, thus enabling the entire fractionation assembly to operate under essentially adiabatic conditions ranging from room temperature to 752°F. This range far surpasses that of any fractionation equipment reported in the literature.

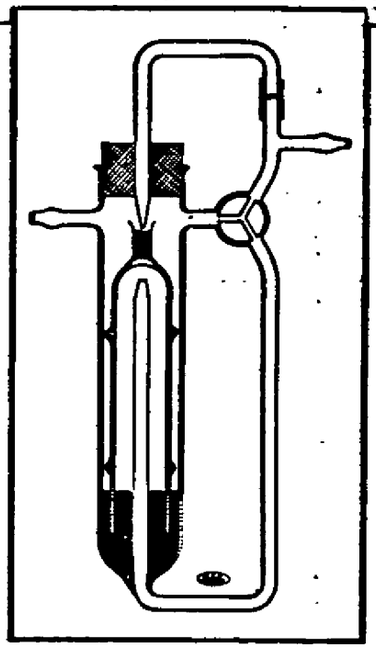
The patented "Staggered Dual Heating Unit" operates this assembly semi-automatically under practically adiabatic conditions for maximum fractionation efficiency with complete visability to all parts of the assembly. This special unit eliminates the necessity of using fragile and expensive silvered jackets which frequently make observations difficult during the fractionation process.

The above and numerous other practical features of this fractionation column assembly not only enable this equipment to be readily operated with very little experience but also make it a generally useful piece of laboratory equipment for all types of simple or complex mixtures requiring precise fractionation in a minimum of time. The numerous practical advantages of this fractionation assembly are well recognized by the hundreds of laboratories presently using this assembly.

CARTESIAN MANOSTAT

IMPROVED MODEL
(Patent Pending)





SUCCESSFUL operation and general acceptance of our first model Cartesian Manostat (over 3,000 in use) has led to the development of a new, more sensitive, completely unitized and mounted instrument.

The Emil Greiner Company, first to offer a regulator that operated purely on a pressure principle, now offers an improved model of that regulator.

The new manostat is mounted on a support and unitized to insure safe handling and easy installation in the laboratory. One three-way stopcock has replaced the two straight bore stopcocks formerly used, which makes for easier manipulation of the instrument.

By increasing the diameter of the float and the float chamber, we have increased the sensitivity to the point where any laboratory system can be held at a constant subatmospheric pressure ranging from 760 mm. of Hg. down to about 1 mm. or less. The sensitivity and capacity of this device has been developed in a recent publication which explains the theory and operations.*

We therefore recommend this device as a most convenient, effective means for obtaining reduced pressure control in vacuum distillations, vapor — liquid equilibrium measurements, etc. This device presents a simple, positive means for setting and maintaining any desired vacuum in a system. It eliminates all electrical appliances and no additional accessories are required other than shown in illustration.

The functioning is explained by the fact that when the pressure is reduced to the desired point in the manostat and system, equal pressure exists within the mercury-sealed bell chamber of the float and outside of it. The mercury therefore is at the same level.

As soon as the stopcock is closed, it is obvious that any evacuation of the system can only be accomplished through the orifice which is now just exactly in contact with the disc.

The leak (not exceeding the capacity of the pump) which may be intentionally introduced now causes increased pressure in the system and consequent mercury displacement downward outside the float and upward inside the float. The float then sinks, opening up the orifice, and permits unrestricted exhaust which then restores equilibrium as the float rises and pushes the disc in contact with the orifice and throttles the effect of the pump as required.

With properly assembled system, smooth accurate control is obtained.

E-1855. Cartesian Manostat, improved model complete as illustrated, made of pyrex glass, mounted on special aluminum support... ea. $27.50

We will welcome your inquiries concerning larger and more sensitive units for special uses.

*For complete details, see article by Roger Gilmont in the October 1946 Analytical Edition of "Industrial and Engineering Chemistry."

The EMIL GREINER Co.

161 SIXTH AVENUE E.G.Co. NEW YORK 13, N. Y.

Branch Office: 112 BROADWAY, CAMBRIDGE, MASSACHUSETTS

O from the methane by boiling pure nitro- under vacuum. The hydrogen stream containing 0.0001 percent CO and 98-99 percent hydrogen is used for the hydrogenation of acetylene to ethylene. The methane stream is returned to the arc unit. The ethane-ethylene stream is charged to a second Linde unit where pure ethylene is separated. The ethane is returned to the arc unit.

The natural gas consumption is 120,000 tons per year. Each 100 kg. of raw gas produces 45 kg. of acetylene, 9.2 kg. of ethylene, 5.3 kg. of carbon black and 142.5 cu.m. of pure hydrogen.

The plant consists of 14 arcs with 12 arcs running at any one time. One arc consumes 7,000 kw. and produces 700-800 kg. of acetylene per hr.

The gas enters the upper section of the arc through a tangential arrangement to produce a swirling motion in the arc tube proper so that the arc will not remain at one point for sufficient time to burn through the tube. The arc tube proper is an iron pipe of 90 mm. inside diameter and 1 m. in length. A water jacket is provided around this tube to prevent excessive burning of the tube. The arc is struck by a starting mechanism which is immediately withdrawn. The iron arc tube has a life of 150 hr. and then is removed and discarded. It is necessary to shut down the arc every 1-3 days for cleaning out the carbon black. Two arcs are used in connection with one water-washing system in order that the arc tube can be cleaned or changed without materially affecting the output of the plant.

HEXAMETHYLENETETRAMINE

THE RAW materials are pumped separately through their own rotameters, in proportion of 3,050 kg. of 27 percent aqua NH_3 to 6,000 kg. of 30 percent formaldehyde, to the mixing chamber. The material is sent from the mixer to the evaporator with 3 compartments containing tube bundles. The dilute solution from the mixer is flowed to the first compartment, and by overflow to the second compartment and by overflow again to the third compartment. The concentrated solution (40 percent solids) is then flowed to a vacuum (150 mm.) evaporator with stirrer in well of tube sheet and with tubes around the circumference. The solution temperature was 60 to 70 deg. C. A vacuum was maintained with a pump and the condensate discharged through a barometric leg. The slurry from the evaporator is discharged to a continuous centrifuge where the hexamine is dried to 5 percent H_2O. There were four such evaporators operated batchwise so that the mixer and concentrator were kept in continuous operation by rotating from one evaporator to another. There were two continuous centrifuges, each with its own steam jacketed dryer. The dryer agitated the product by a rotating screw similar to a screw conveyor. The hexamine containing 5 percent was discharged into the dryers described above where the steam jacket maintained a temperature of 105 deg. C. inside of the dryer. The hexamine was put through a crusher and screened to size with oversize lumps returned to the crusher. The product (99.9 percent hexamine) was bagged as made into 100 kg. bags with a weighing device on the end of the dryer after the crusher. The

mother liquor from the centrifuge was run to a stirring kettle, diluted with water, and charcoal was added to remove the color. The solution was then allowed to settle and the clear liquor pumped back to the concentrator for reprocessing.

THE FISCHER-TROPSCH PROCESS

In the first few days of March 1945 a Fishcher-Tropsch plant at Moers and a hydrogenation plant at Wesseling were captured and opened for investigation. An I. G. Farbenindustrie plant at Ludwigshafen was captured on March 23.

Since the synthetic oil industry was the basis for most of the military and civilian transportation, it received a great deal of attention from the Allied bombers. German synthetic production reached a peak of, somewhat over 350,000 metric tons per month in 1944.

The first Fischer-Tropsch plant investigated was at Moers, a small town east of Krefeld, on the west bank of the Rhine. All other Fischer-Tropsch plants were in the Ruhr (exclusive of those which may exist in the areas seized by the Russians) with the exception of a commercial plant at Lutzkendorf and one small pilot plant near Leipzig. Information on plant operations was not difficult to secure.

All Fischer-Tropsch plants in Germany operated by essentially the same process, with only minor variations. In fact, no Fischer-Tropsch plant has been built since 1938, a decision which hinged apparently on the German conviction that they would be able to seize other sources of oil, and did not need to expend additional funds, manpower, and material for synthetic oil plants.

Synthesis gas for the plants was made almost universally by the water-gas reaction, using coke. Experimental work using brown coal as raw material was being tried in the Leipzig area. Purification of the gases was carried out in two steps using iron oxide catalysts to remove H_2S and iron oxide catalysts treated with sodium carbonate to remove organic sulphur. In the latter case a small amount of oxygen was bled into the gas before purification was attempted. The ratio of hydrogen to carbon monoxide was balanced by the use of a shift converter to react CO and water to produce hydrogen on by means of cracking coke-oven gas thermally or catalytically. Where coke-oven gas was used, an active carbon adsorption system was frequently necessary to remove resinous material. This step generally preceded passage of the gas to the organic sulphur removal equipment.

At Moers the plant contains three batteries of coke ovens of which the two oldest were built in 1907-08 and the newest was built in 1928-29. There are 210 ovens in all. The newer ovens handle 20 tons of coal per charge, which is coked in 32 hr. The normal throughput of all ovens was 1,800 tons of coal per day which yielded 1,500 tons of coke per day.

Water gas is made from coke in 11 Koppers generators and is passed in part through a catalytic convertor unit to increase the ratio of hydrogen to carbon monoxide. Coke-oven gas is "cracked" with steam non-catalytically in a battery of six Cowper stoves and is mixed with converted water gas in the proportion required to give a 2¾:1 ratio of hydrogen to CO. The mixed

6/6 15°

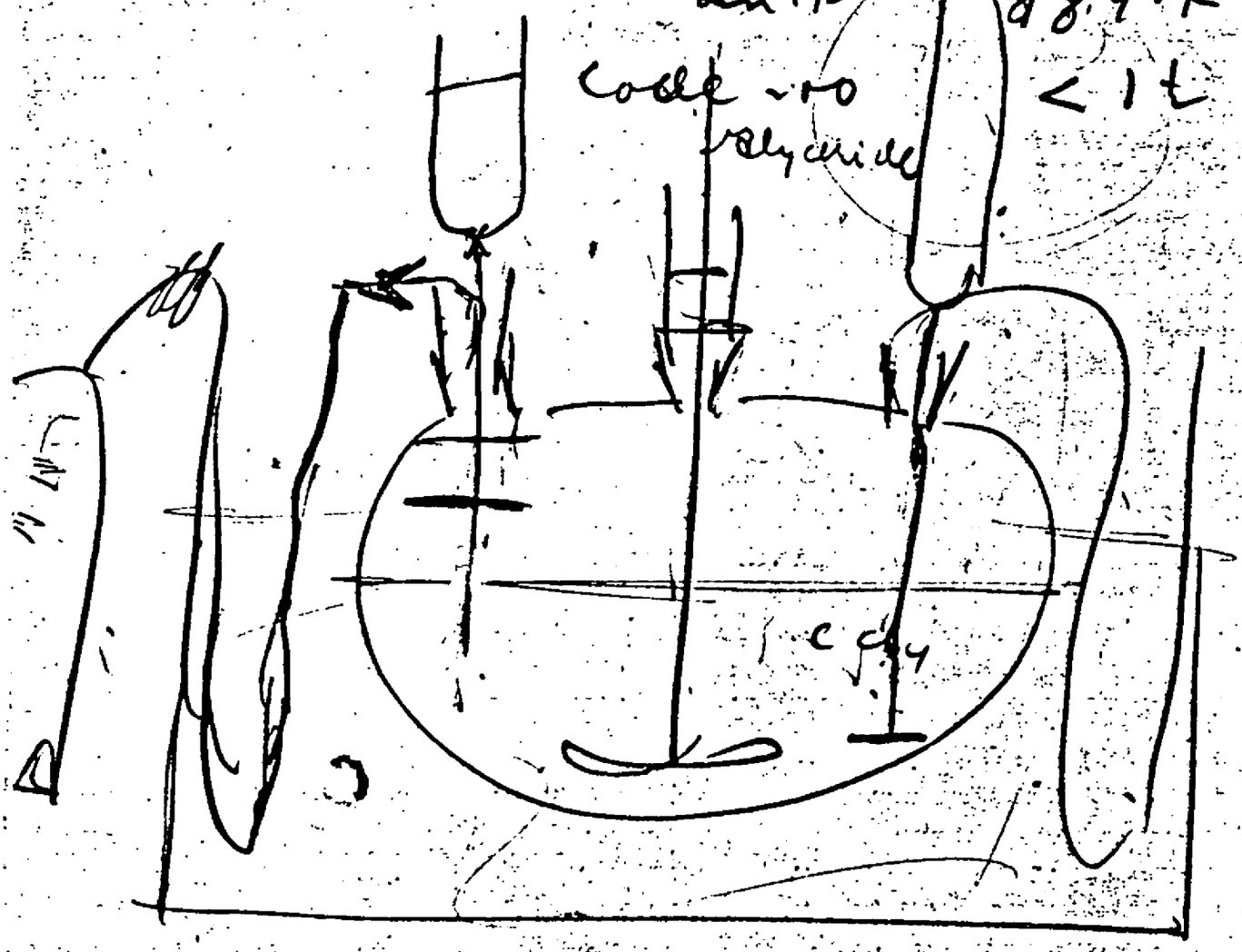
Conditions

-10°C

60 & 40 CCl_4
C_6H_6

156°F
code 150-H
and NO < 1

Total
an. P 88.9°F
code -10 < 1t
polymide



G 3 L 1

(R)

65-4307

Ex 12 E

Evaporation with C_2H_5

Distillation

Time	Bath °C	Catch °C	Inner Column Therm °C	Upper Column Therm °C	Pres. mm.	Remarks
1:27	162	117.5	83.5	64.3	Atm.	
1:35	166	122.5	87.3	64.2	Atm.	
1:42	173	131	93	63.5	Atm.	
1:53	187	140	93	65.0	Atm.	
2:00				66.0	1st Cut 36 g. product	
2:17	192	148	86	—	Atm.	
2:20	195	151	92	63.5	Atm	Low Readings due to broken equilibrium
2:30	198	155	97	63.0	Atm.	Broken film ascending
2:37	203	159	103	63.0	Atm.	—
2:48	210	163	113	65.2	Atm.	Add material 1st cut
			Temp at top of column rose rapidly as "broken film" left top of column			
2:55	214	166	117	71.0	Atm.	Temp. steady
3:00	216	167	118	71.0	Atm.	
3:10	218	168	120	68.5 (?)	Atm.	

Cetrification with P_2O_5 2-28-4

Sheet I

Used

26 cms. 0.0 H acid

32 cms. MeOH (+ 25(?) cms. additional)

24 cms. P_2O_5

some charring obtained

refluxed for 3 hrs.

Distillation

Time	Bath °C	Lower Col Batch	Lower Col °C	Upper Col °C	Press.	Notes
:00	[illegible]	55	35	25	Atm.	1st drops on neck of flask
:20	–	54	36	24	Atm.	Lower therm liquid covered (Dimethyl ether?)
:35	100	85	63 (to 66 in 2 minutes)	23	Atm	Initial boiling in flask. Then temp. drops to 81 C in flask.
:55	128	84	68.7	63	Atm	1st Condensate
:05	128	86	69.2	63	Atm	
:35	134	90	71	64	Atm.	
:45	137	94	71	64	Atm.	
2:53	140	96	72	64.3	Atm.	
:00	143	100	73	64.2	Atm.	

((2) (3-10-19

Concentrations of p. Toluene sulfonic acid

yields

1st Fract. (Melt)	[illegible]
2nd Fract.	[illegible]
3rd Fract.	[illegible]
4th Fract.	[illegible]

#2 [illegible] Cu 0 [illegible]

			1.2.5-47
			153.8
Fract 1	L	50-55°C	85.6
	V	56-65°C	48.2 g.
	A	65-77°C	
Fract 2		55-60	92.5
		65-68	76.0
		77-85	16.5
Fracts 3 & 4		60-65	109.1
		68-83	91.1
		85-110	17.0
Fract 4		65-71	91.0
		73-95	86.5
		110-153	4.5
Fract 5		133-191	119.1
			79.4
			39.6

Cu?

Res. ? 3.62 g.

(3 0 6 - 4 7

3 40 9 . Pr 0 5

[illegible] 1	V	50-55	169.3
	L	63-70	92.1
	P	65-115	77.2

[illegible] 2	V	55-60	93.2
	L	70-91	77.0
	P	115-160	16.2

[illegible] 3	V	60-65	101.1
	L	90-130	76.0
	P	160-300	25.1
			+ 1.5
			26.8

Are Me
60 20 Me Me

Res. 60.9 gm.

[illegible]	[illegible]	
[illegible] 1	50-55 57-65 68-78	170.0 82.3 87.7
[illegible] 2	55-60 65-73 78-95	98.9 80.0 18.9
[illegible] 3	60-65 73-105 95-130	89.3 77.0 12.3
[illegible] 4	65-90 105-140 130-160	89.3 80.0 9.3
[illegible] 5	140-[illegible] 160-300+	93.8 51.8 32.0

7070 MAME
= [illegible] 9.

Res

30.69

Extraction MeCEt

→ 0

#5 [illegible] 10 [illegible]

well 1 { L [illegible] / P [illegible] } [illegible]

well 2 { L [illegible] / P [illegible] } [illegible] g.

well 3 { P [illegible] } [illegible] g. [illegible]

[illegible] Fact 1 [illegible] g sample

[illegible]

[illegible]

Res. [illegible] g.

4-2-47

#6 [illegible] 6 [illegible] MeOH Refluxing

act 1 { 23-60, 60-75, 75-105 } 180.9 − 91.1 = 89.8 gm.

act 2 { 60-65, 77-83, 105-120 } 93.7 − 77.2 = 16.6

act 3 { 60-65, 83-85, 120-133 } 83.4 − 79.2 = 3.2

act 4 { N —, L 85-120, P 133-162 } 109.6 − 36.3 = 22.8

act 5 { N —, L —, P 163-188 + Vac } 63.1 − 55.0 = 33.1 − 3.7 = 16.8

Res 25.9 gm.

8

[illegible] 1	50 – 65 55 – 90 65 – 130	182.9 84.8 98.4
[illegible] 2	65 – 76 95 – 120 130 – 166	67.8 54.9 12.9
[illegible] 3	166 – 190	110.5 80.7 29.8

[illegible]

286.1
244.2
41.8

98.7
12.9
29.8
184.4

17.9
17.6

run #7 { 80 cm CHCl3
40 cm α-OH acid

(4-4-47)

[illegible] during
reaction

Date	added	Loss	Time
244.2 tare			
80.0 CHCl3			
40.0 α-OH acid			
364.2			
after α-OH acid is dissolved, wt is		1.9	
362.3			
364.2			
20.1 ← Pr OS			3 40/PM
384.2 total			
384.2			
379.5		5.7	5 40/PM
5.7			
			5 22/PM

100 cm
40°

Lab Program ① 4-7-47

Chel Processing

A. Prepolymerization

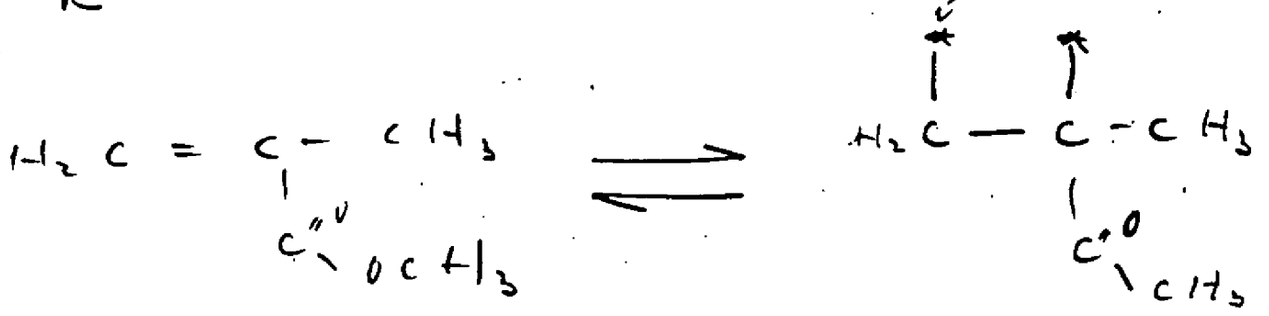
$$R-C(=O)-O-O-C(=O)-R \rightleftharpoons 2[R\cdot COO]$$

$$[RCOO]^- \longrightarrow R^+ + CO_2$$

$$R^+ + RCOO^- \longrightarrow RCOOR$$

$$R^+ + R^+ \longrightarrow R-R$$

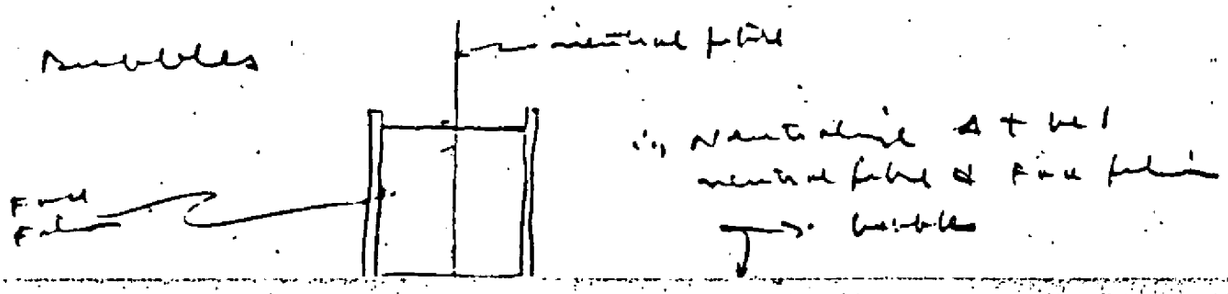
Reduced by R



✓ = competition point

1. competition bet reactions
2. the higher the temp., the greater the possibility of chain termination.
3. use least max period of 2°/min.

5. Bubbles



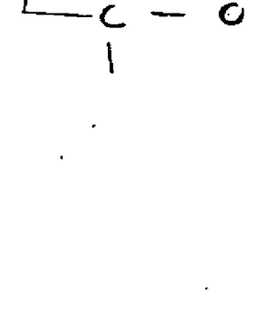
C (3) O 4-7-47

4 mechanism of Ozonolysis

atomic oxygen

$$O_3 \longrightarrow O_2 + O$$

$$H_2O_2 \longrightarrow H_2O + O$$



Tare	444.2	
14 cls	80.0	
	344.2	7 10
add-on	40	7 40
	384.2	7 40
	20	
	364.2	7 40
		8 00
	404.2	
		8 15
	444.2	
		8 20
	444.2	
		9 20
	464.2	

ajk.

[illegible] DOCK

[illegible]

[illegible] 1	[illegible]	[illegible]	
	[illegible]	[illegible]	
	[illegible]		
[illegible] 2		[illegible]	
		[illegible]	
[illegible] 3		[illegible]	
		[illegible]	6070 [illegible]
[illegible] 4		[illegible]	
		[illegible]	
		12.0	

[illegible] 1913 [illegible].

4-12-47

Production of Me Mb from α-OH acid

by means of $POCl_3$

charge

α-OH acid	40 gms.
$CHCl_3$	120 gms.
$POCl_3$	21 gms.

Tare 244.2
40.0
120.0 + 40 + 80
524.2

$POCl_3$ additions

~~Time Bath Flask amt added~~

0

Run in about ½ no reaction

raised gradually to 53°C → reaction

added rest of $POCl_3$ → ~~[illegible]~~ nearly done at

total wt after overnight reaction

473.7
51.1
524.7

wt after refluxing with MeOH

524.7
522.5
2.2 loss (?) [illegible]

4-12-47

5 Condensation on α-OH acid

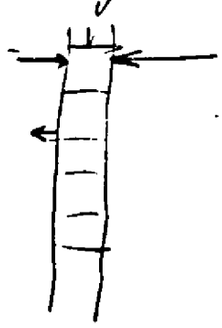
Contact between reagent & solution of α-OH acid

- 60° P_2O_5 — Heavy tars — 70-80% yields
- 55°C $POCl_3$ — no tars — 50% yield
- 80°C P_2O_5 — no tars — 10% yield

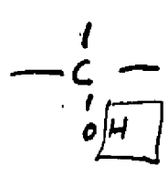
- addition of 4 moles MeOH to α-OH acid — 60°C — 6 hrs.
- stripping of solvent — 150°C
- refluxing operation — 150°C — 12-2 hrs.
- Distillation of product

is known $(H_3C)_3PO_4$ mechanism.

no such thing as a strictly neutral bond



we have a tertiary alc.



& we demand that OH act as a base.

4-14-09

Made via $POCl_3$ - $(CH_3)_3PO_4$

charge { 50 cm MeOH
39.4 cm $POCl_3$

stock TAA

269.2
50.0 MeOH
319.2

added $POCl_3$ slowly 1:00 – 1:25 PM
keep t° @ 0°C.
Vac on at 2:50 50 ——— t° = 15 – 21°C
Vac off at 4:50 50 ——— t° = ~4°C

Wt 308.5

93
31
16
130

130
153.4 × 39.4 = 33.4
269.2
302.6
~~28.0~~
~~327.6~~

MeOH used no sign.

added α-OH acid & MeOH

37.5
40.0
77.5 cm

308.5
77.5
385.0

added α-OH acid diss in MeOH
8 Fr 383.6

4-15-47

1-OH → MeMgI Reaction via Ether-Rx

Charge { 160 gms. Et-O
40 gms.
20 gms Rx OH

Total added

160
40
20
50
270

Total 269.2
Total 489.2

160
46
196

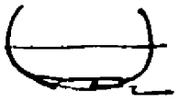
Start 2 hrs
Boiling 3 hrs
Reboiling 4 hrs

check on wt. 490.2 18 hrs 4-16-47

continue reaction for 8 hrs 4/16 — wt. 486.3
(some still on bottom)

added 50 gms. MeOH (after cooling Rx OH)

→ emulsion → layer


dark layer

Total wt. 486.3
50.0
536.3 removed at 39°C

∴ check on wt after ~~some~~ some removed @ 39°C

∴ distilled off Et-O → 6 hrs 71°C — 6 hrs

298.7
151.5 Cu
147.2 ... 149.1

~~289.7~~ 269.2
1 > 0.5

290.1 ⟷ 290.1 O.K. 11 hrs

[illegible] distilled H_2O { V 60 - 65 / L 70 - 90 / P 91 - 130 }

106.7
[illegible]
346

wt. 353.9
[illegible]
87.6

[illegible] returned 1 $\frac{10}{AM}$ to [illegible] $\frac{10}{PM}$

353.9
[illegible]
34.7

141. 39.1 am { 130 - 210

[illegible] 5.8 am { [illegible]10 - [illegible]11

[illegible]97.5
[illegible]69[illegible]
28.3

28.3
73.2
residual

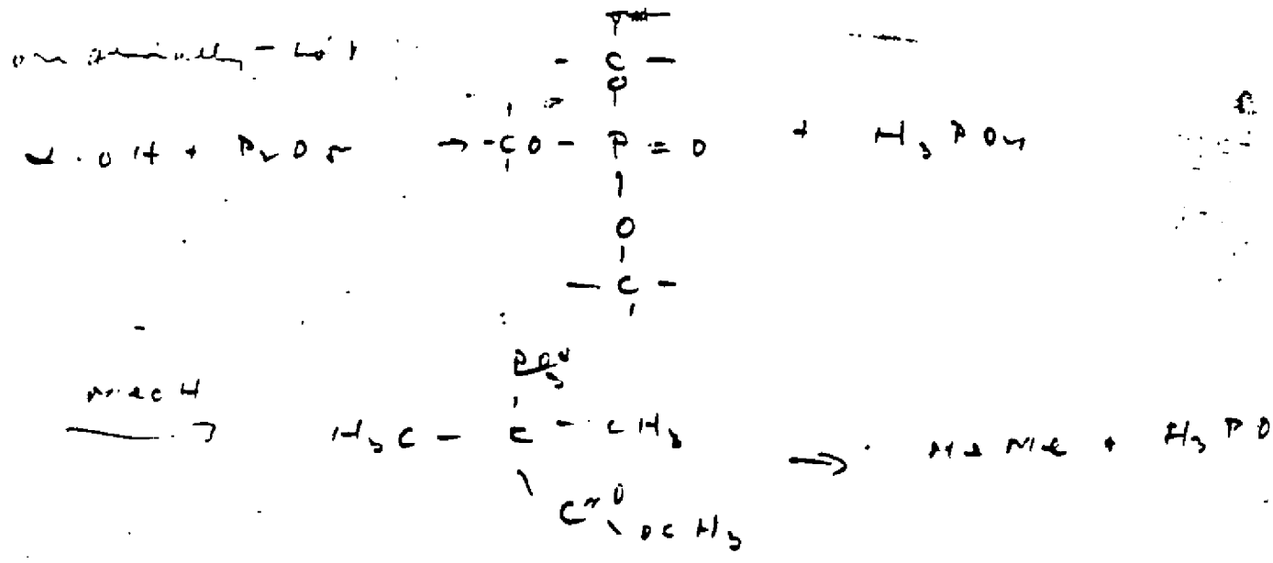
73.2

[illegible]
[illegible]
[illegible]
[illegible]
[illegible]
[illegible]

4-17-47

meeting/ α C-OH acid → MeOH

on [illegible] – Lo'l



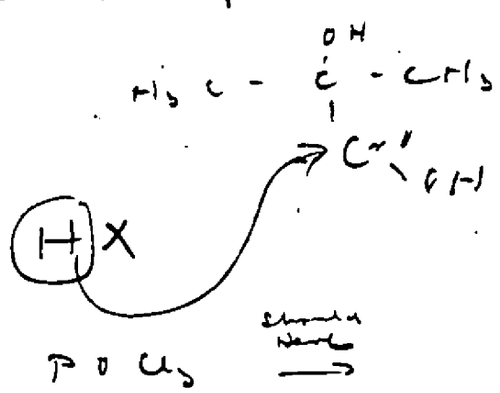
2 α-OH → Lactide $\xrightarrow{MeOH}$ [illegible]

α-OH ester $\xrightarrow{H_3PO_4}$ MeMe

α-OH → Polymer $\xrightarrow{MeOH}$ α-OH ester

$\xrightarrow{H_3PO_4}$ MeMe

Dehydration α-OH acid



-1. $POCl_3$ $\xrightarrow{\text{[illegible]}}$ P=O ester

50-85%
[illegible]

(③) 4-17-47

Summary

1. H_3PO_4 [illegible] → decomp.
2. react goes at [illegible] temp.
3. $POCl_3$ on q
4. Reaction goes at interface

① 4-20-47

Preparation of MCMC from α-OH isobutyric acid via PCl_5 @ -10°C

Charge
- 160 gms. $CHCl_3$ (+80)
- 40 gms. α-OH acid
- 36 gms. PCl_5

$\frac{137.4}{104} \times 0.667 \times 40 = 35.3$ gms. PCl_5

Take off flask = 234.8
280.0
514.8

Reaction Data

Time	°C	Wt	Notes
1 PM	-10	514.8	no reaction
1 PM	-5	—	no reaction
1 45	0	—	no reaction
2 00	10	—	no reaction
3 00	25	—	some reaction
3 20	40	—	HCl evolution about 20 gms. min
4 20	40	—	all in
5 PM	40	—	0/40°C for 1 hr

(3) 4-21-47

time	°C	wt	Notes
10 30 AM	61	589.1	565.2 539.1 27.1

no odor of MeMe
yellow color

Distillation

1st Fraction	V	50-55	301.5
	L	55-80	77.7
	P	67-132	222.7
2nd Fraction	V	55-65	100.6
	L	80-95	81.0
	P	130-180	19.6
3rd Fraction	V	—	111.9
	L	95-155	81.7
	P	180-200 (260)	30.2
		methylurea	= 20

→ 66.70 MeMe

Residue	257.3 234.9 22.5	222.7 19.6 30.2 22.5 295.0

519.1

PO4 464.0 mg 4-25-47
460.9
3.3

Oscillation Record

act	V 64 – 67		89.2
	L 69 – 83		71.3
	P 104 – 147		17.9

act	V 67 – 65		79.5
	L 83 – 140		67.2
	P 147 – 190		

	mg	200	400	400
act	V	90	90	86
	L	140	127	125
	P	195	205	206

9.5

553.0
187.0
672.2 amp.
17.9
9.5
94.6 amp.

100
30
40
50
120

4.23.47

Recovery of MeMe from a $CHCl_3$ - MeOH azeotrope column.

Charge

258.0 gms. $CHCl_3$	
37.2 gms. MeOH	
38.5 gms. MeMe	
333.5	

Total

263.7	
257.0 $CHCl_3$	
521.8	
37.2 MeOH	
559.0	
38.5 MeMe	
597.5	

residue

741.3
258.0
16.3
150.2
119.3
54.4
15.0

Distillation

Fract. 1

V	39 - 55	194.2
L	55 - 58	69.0
P	63 - 65	150.2

Fract. 2

V	55 - 56 - 65	193.7
L	58 - 61 - 76	74.5
P	65 - 70 - 85	119.3

Fract. 3

V	65 - 75?	107.5
L	76 - 98	55.1
		52.4

4-28-47

recovery of MeNH from an $CHCl_3$ - MeOH solution

Charged
- 80.0 gm. $CHCl_3$
- 37.2 gm. MeOH
- 38.5 gm. MeNH

155.7

Tare

238.0
- 80.0 $CHCl_3$

318.0
- 37.2 MeOH

355.2
- 38.5 MeNH

393.7

Residue

248.2
- 238.0

10.2
30.1
77.7
17.6
16.0

151.0

Distillation

1st Fract.
- V 50 - 55
- L 58 - 67
- P 69 - 83

110.1
- 80.0 Tare

30.1

2nd Fract.
- V 55 - 70 - 77 - 85
- L 67 - 81 - 85 - 95
- P 93 - 90 - 96 - 99

151.3
- 73.6 Tare

77.7

4th Fract.
- V 85 - 88 - 91 - ?
- L 95 - 99 - 99 - 100
- P 99 - 100 - 101 - 102

83.2
- 65.6

17.6

4-22-47

Recovery of MeMe from $CHCl_3$ - H_3PO_4 mixture.

1. Charge
- 80.0 gm $CHCl_3$
- 48.7 gm H_3PO_4 (85%)
- 38.5 gm MeMe
- 37.2 gm CH_3OH

204.4

2. Tare

244.3
80.0 gm $CHCl_3$
324.3
48.7 gm H_3PO_4
373.0
38.5
411.5
37.2
448.7

3. Distillation

1st Fraction	50 - 55	139.0	Does not recolorize KMnO4
	58 - 62	85.7	
	67 - 90	53.3	
2nd Fraction	55 - 70	146.0	Recolorizes KMnO4 strongly
	62 - 82	80.2	
	90 - 120	65.8	
3rd Fraction	70 - 83	102.0	
	82 - 125	77.1	

Fault 4

V	78 - 83	95.7
L	78 - 85	76.1
P	[illegible]	17.6

Fault 5

V	83 - 88	76.0
L	85 - 92	[illegible]
P	100 - 199	[illegible]
	(sum)	= [illegible]

Residue

309.5
268.2
41.3

C O 4-22-47

Recovery of MeMe from a $CHCl_3$ - H_3PO_4 mix

Charge

120.0 gm	$CHCl_3$
48.7 gm	H_3PO_4 (85%)
37.5 gm	MeMe
37.2 gm	CH_3OH
244.4	

Total

268.2	
120.0	$CHCl_3$
388.2	
+ 48.7	H_3PO_4
436.9	
37.5	MeMe
474.4	
37.2	
512.6	

Distillation

Fraction 1	V	50 - 55	159.8
	L	54 - 68	73.1
	P	65 - 100	86.7
Fraction 2	V	55 - 65	154.2
	L	68 - 70	86.8
	P	100 - 110	47.4
Fraction 3	V	65 - 70	88.4
	L	70 - 78	75.7

(① ( ) ; 4-60-47

Preparation of Me Me from α-OH hydrogenic acid via P_2O_5 @ 50°C

Charge
- 90 gms. CH_2Cl_2 (= 45)
- 41 gms. α-OH acid
- 20 gms. P_2O_5 + 10 gms. P_2O_5

Tare of flask 244.6
180.0
424.6

Reaction Data

Time	°C	Wt.	Notes
9 45 AM	50	424.6	start
10 45 AM	50	424.2	no sign of reaction
11 45	50	423.9	no sign of reaction
12 00	50	—	some signs of liquefaction
1 45	50	423.6	slight liquefaction
2 45	50	423.0	swelling → sticking on sides
4 45	50	422.8	
11 45 PM	50	422.4	liquid except for sides
12 45 AM	50	422.4	added 10 gms P_2O_5
1 AM	50	—	sticky on sides
2 30 AM	48	—	sticky on sides
		420.9	mostly fluid

4-44-47

Lot @ 50°C

time	°C	wt	Note
3 PM	50	431.0	add NaOH flakes.
		491.0	
1 - 7 AM	63	480.3	replace for 13 hrs.

4. Distillation

1st Fract
- V 50 - 55
- L 56 - 93
- P 65 - 130

233.8
80.1
138.7

2nd Fract
- V 55 - 95
- L 93 - 110
- P 130 - 167

92.0
78.0
14.0

3rd Fract
- V —
- L 110 - 155
- P 167 - 210

144.8
91.4
53.4 (0.64)

40.1
3.8
43.9

Residue

484.8
444.6
40.2

5-6-47

Quantities

200 ml chloroform
45 g α-hydroxyisobutyric acid
29 ml chlorsulfonic acid
57 g methanol

11:00 started adding chlorsulf. -20°C
30 finished " "

1:10 started adding methanol N-20°C
30 finished " "

2:00-3:00 reflux - temp 52-58°C

Distillation

Temperatures:

	Still Pot	L.C.	Vapor	Variac
Time 5:20	61 °C	52 °C	—	32
45	62	56	51 °C	40

1st Fract
N 50 - 55
L 56 - 68
P 62 - 90

350.2
76.0
278.2

2 Fract
90 - 130

116.7
76.8
29.9

3 Fract
130 - 134 (max) - [illegible] (clear)

111.0
76.1
34.9

+ 5 Vac

C

() varial

Vaar 50 - 55

L.C. 57 - 63 (30)

Full Pat 65 - 90

Vaar 55 - 61

L.C. 63 - 80 (20)

Full Pat 90 - 120

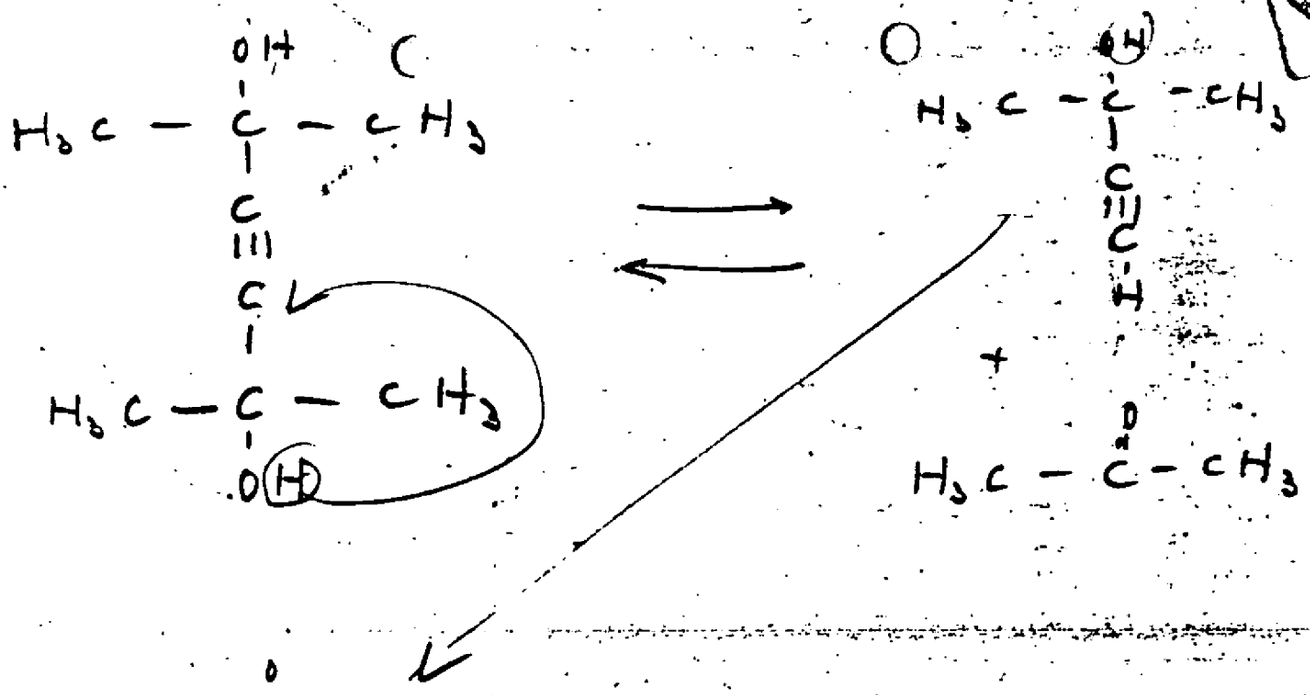
Vaar

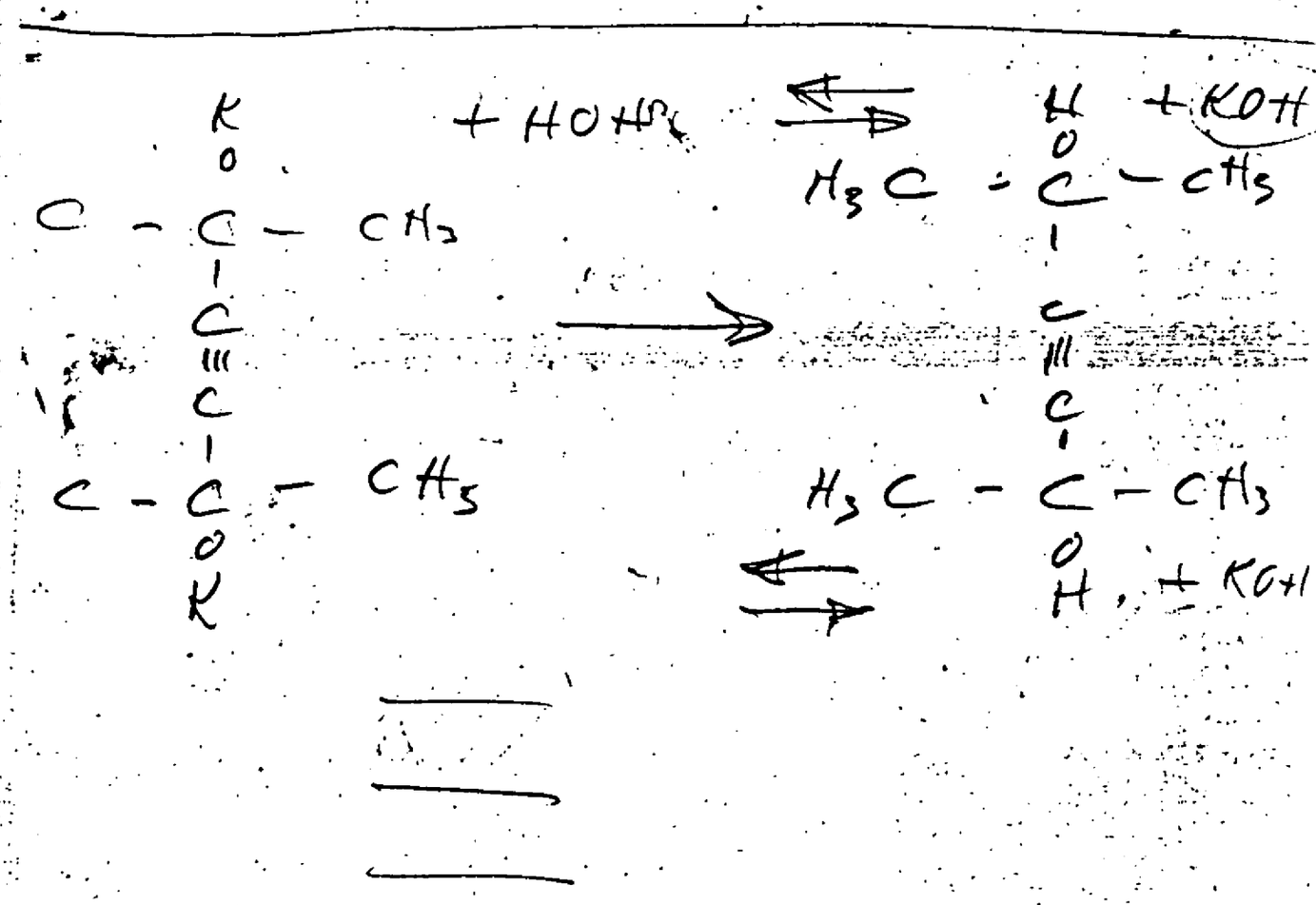
L.C. (60)

Full Pat 120 - 163

Full Pat 163 - 190 185 (72)

Vol





1.16.50

5-9-49

α-OH - chloroacetic acid [illegible] ()
steam distilled @ 135°C

11:00 started adding $ClCO_2H$ (@ -20°C)
11:35 all fluid (two phase) (18 cc in)
12:05 [illegible] @ -20°C - still fluid
12:15 added [illegible] of $ClCO_2H$
12:17 warm solid - suddenly
1:17 cold H -20°C [illegible]

1:35-1:53 add CH_3OH (@ +15°C)

2:10-3:10 Refluxing

	Still Pot	Vapor	Variac
3:10	61	—	—
6:15	63	54½	45
7:05	66	53	45

1st Fract { V 50 - 55 ; P 63 - 90 } 31.9 + 80.9 = 51.9

2nd Fract { V 55 - 65 ; P 90 - 133 } 12.4 + 90.7 = 49.4

3rd Fract { V 65 - 100 ; P 130 - 135 (steam distilled) } < see memo

4th Fract { P 135 - 190 → 140.4 }
[illegible]
1 [illegible]
(Ave 04 [illegible])

2-OH-[illegible] Acid [illegible] (0-20°C) 5-7-47
[illegible] Bottle @ 135°C

1:00 Started adding Chlorsulfonic Acid
1:20 Finished "
2:20 Raised temp to 15°C by 12:50
2:50 Start adding Alc
1:10 Finished "

2:00 - 3:00 Reflux

3:50 Distillation begins

Temperatures

	Still Pot	Vapors
3:50	65½	53½°C
4:10	65½	54°C
4:45	73	55

Added some Cu powder

V 53 - 55
P 65 - 98

363.9
75.7 — $MeCl_2O$
288.2

V 55 - 70
P 98 - 150

92.8 — trace $MeCl_2O$
80.6
12.2

V 70 - 62 - 99
P 150 - 160 - 170 - 153
increased
should not have been permitted

79.5 — [illegible]

Some $MeCl_2O$ (170-220)

.16 cc ≈ 16 [illegible]
[illegible]

[illegible] p. 215

[illegible] equil. const. of esterification is only slightly affected by the structure of the acid or alc.

Acids in [illegible]

Relative rates of esterification

R COOH in MeOH

R = CH_3 = 1

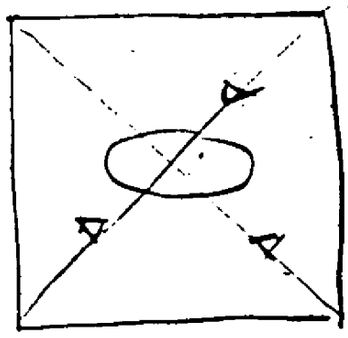
i-C_3H_7 = 0.54

t-C_4H_9 = 0.005

6/6/50

(②) 4-7-47

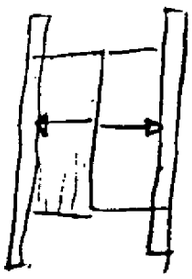
C. Ratio of Cd surface area to Face area



case a higher to α areas ahead → arrow-like bubbles.

Vapor goes out → arrowlike bubbles

D. Getting rid of stresses – annealing



should need diff times for diff. thicknesses of sheet.

During the annealing period the temp should be as near to softening point as possible.

I methacrylate Synthesis

A. Acetone Synthesis – control C_2H_2 addition

B. oxidation of Acetone

1. Acetone KMnO4 → α-OH acid → acetone + formic acid + CO_2

2. NH_3 → 0

3. Fe SO4 + H_2O_2 → 0.770 (@ 70°C for 4 hrs).

1. need high t° for C=C. while KMnO4 takes α-OH at about 0°

1. need from more unsaturated the α-OH group. So alt ketone

65-4307

Ex 12 F

Continuation sheet no. 1 ()

Harry Gold 6823 Kindred St., Phila. 24, Pa.

Born Dec. 12, 1910 Chemist, P6

Item 16. Experience

May, 1946 to Present

1. The improved methyl methacrylate monomer synthesis (mentioned on Form 57) involves a novel method which eliminates the use of HCN and which will be far more economical. Within two or three months an article by Mr. Rothman and myself will be published in Chemical and Metallurgical Engineering which will give some of the details of the process.

2. The work on methyl methacrylate and Polystyrene molding powders was undertaken to develop unique methods of emulsion polymerization which do not conflict with any of those already patented.

All of the above work was done under contract to the "Commission on Aeronautical Affairs of the Republic of China".

3. The work on Vitamins B_1 (Thiamin), B_2 (Riboflavin), and C (ascorbic acid) was undertaken with the purpose of developing more economical methods of synthesis. Although most of the effort has been expended in Library research, the Laboratory work done thus far has indicated definite signs of success.

65-4307

Ex 12 G

The oxidation of Derivatives of acetylenic alcohols and glycols

I. Statement of Invention

This invention relates to a process for the oxidation of ~~ether or~~ ester derivatives of acetylenic alcohols or glycols to produce the corresponding ~~ether~~ or ester aliphatic acids; more specifically it concerns the production of α-ether or ester aliphatic acid from ~~ether or~~ ester derivatives of acetylenic alcohols or glycols employing oxygen as a means of splitting the triple bond and introducing oxygen into the molecule.

The ~~α-ether or~~ α-ester aliphatic acids obtained are valuable as both starting and intermediate materials in organic syntheses. Special reference is had to the use of these acids, particularly ~~α-methoxy~~ ~~butyric acid and~~ α-acetoxy isobutyric acid, in procedures for the manufacture of monomeric acrylic esters, particularly methyl methacrylate, as described in co-pending patent applications

II. Prior art

A. Statement

The literature records just one attempt at the oxidation of ~~ether~~ ester derivatives of acetylenic glycols and none for ~~ether~~ ester derivatives of acetylenic alcohols. A. Du Pont {Comptes rendus 150, p. 1523 to 1525 (1910)}, used 2 to 3% $KMnO_4$ and H_2SO_4 on 2,5-Dimethyl-2,5-Dimethoxy-Hexine-3 and 2,5-Dimethyl-2,5-Diacetoxy-Hexine-3 at low temperatures, employing acetone as a solvent and using an excess of $KMnO_4$. Du Pont reported the yields as "satisfactory" but states that the oxidation takes several days and also that the acetone is attacked.

B. Critique

In the same investigation, Du Pont had made a prior effort to oxidize 2,5-Dimethyl-2,5-Dihydroxy-Hexine-3 to α-hydroxy isobutyric acid using the same reagents and conditions as for ~~the methoxy and~~ acetoxy derivatives and he obtained very poor yields plus a great amount of acetone and oxalic acid. He

the difficulty was the lability of the OH group of the α-hydroxy isobutyric acid as it was formed and this occurrence has been amply verified by other workers in the field. Thus, it was to 'protect' this vulnerable OH group that DuPont carried out the oxidation on the methoxy and acetoxy derivatives of the acetylenic glycol. There are three faults with DuPont's method:

1. The oxidation time of 'several days' is too long for the process to be commercially feasible.
2. a considerable excess of the $KMnO_4$-H_2SO_4 reagent is needed.
3. Under the conditions '1' and '2' above, the acetone used as a solvent for the reaction is itself attacked.

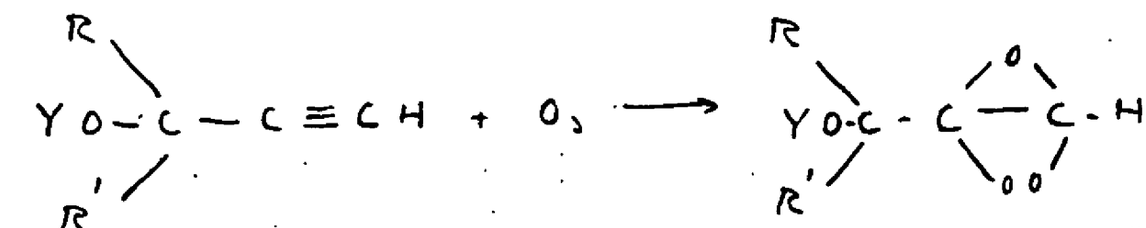
III. Novelty

A. Theory

Our invention is based in part on the fact that ~~an ether or~~ ester substituted derivative of an acetylenic alcohol or acetylenic glycol will quantitatively and completely absorb ozone to yield an ozonide. This ozonide can then be

split by the action of water to produce the corresponding ~~α-ether or~~ ester aliphatic acid. Thus,

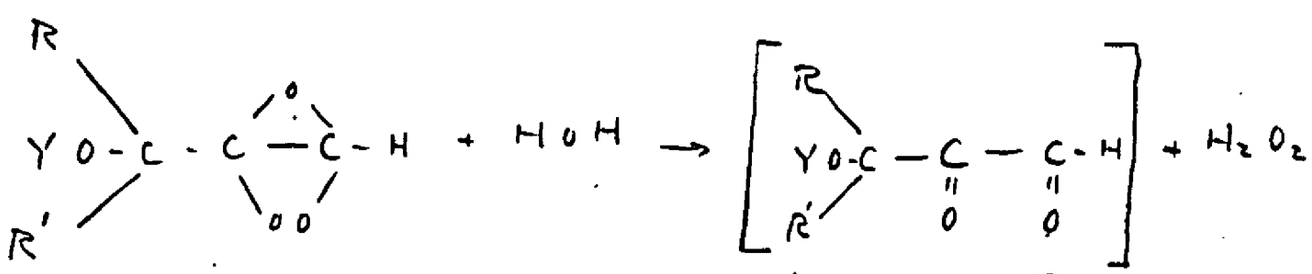
1. In the case of an ~~ether or~~ ester substituted derivative of an acetylenic alcohol,



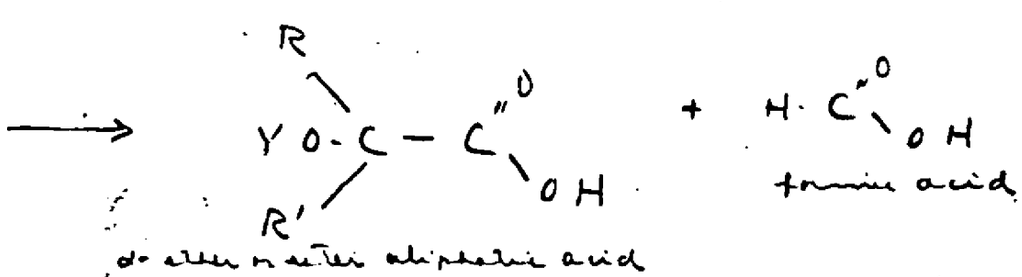
ester or ester derivative of acetylenic alcohol

ozonide of ether or ester derivative of acetylenic alcohol

then,



α-diketone derivative of acetylenic alcohol



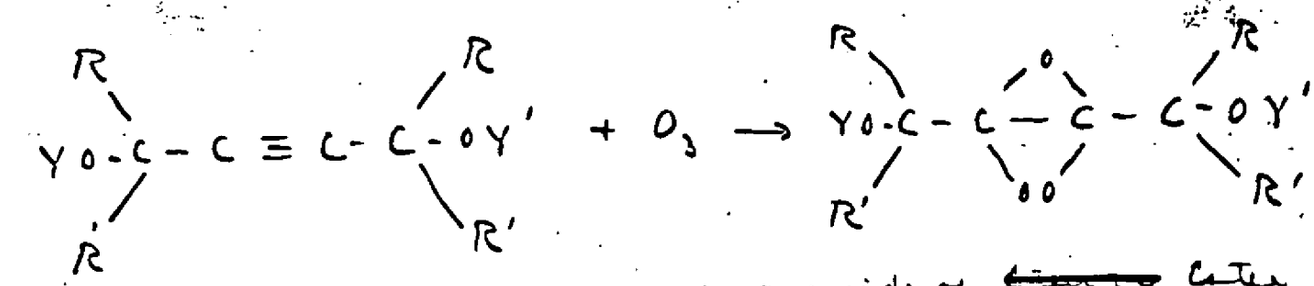
α-ester or ester aliphatic acid

formic acid

where R and R′ may be the same or different alkyl radicals or may be H atoms and Y is ~~either an alkyl~~

~~group of~~ acyl group, $R-C(=O)-$.

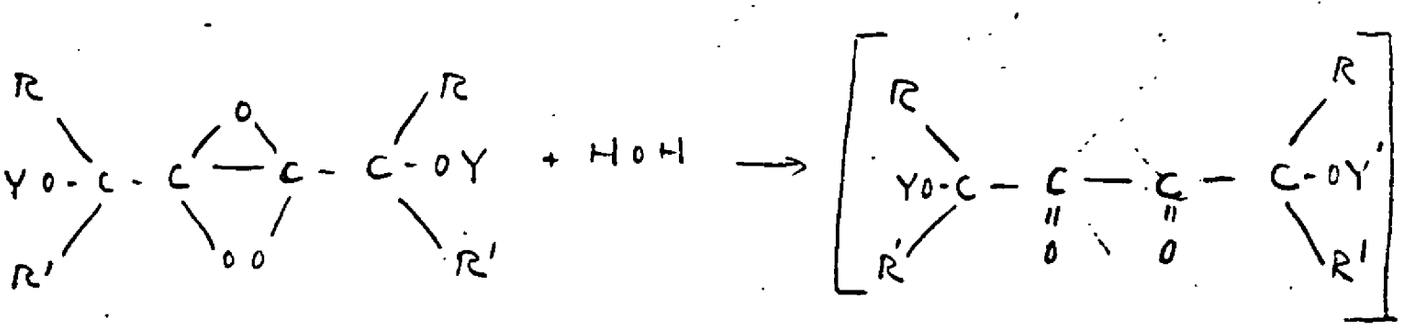
2. For an ~~[illegible]~~ ester ~~substituted~~ derivative of an acetylenic glycol



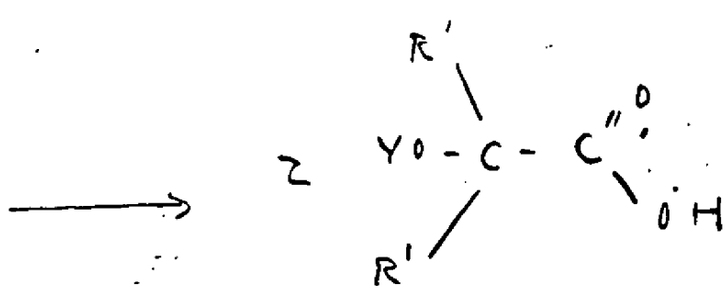
~~[illegible]~~ Ester derivative of acetylenic glycol

ozonide of ~~[illegible]~~ ester derivative of acetylenic glycol

then,



$+ H_2O_2$



where R and R' may be the same or different alkyl radicals or may be H atoms and Y and Y' may be the same or

different ~~alkyl groups as~~ acid groups, $R-C(=O)-$.

So far as we are aware there are no known instances of the use of ozone to transform ~~esters or~~ ester derivatives of acetylenic alcohols or glycols to ~~acetylenic~~ ester aliphatic acids. Also, we believe that this invention and that described in co-pending patent application

to be the first commercially feasible methods for the production of useful synthetic organic chemicals via the ozonization of the triple bond. This is due in part to the high yields obtained and in part to the lack for the need of the special precautions usually employed in the ozonization reactions and in the avoidance of many difficulties such as

a. abnormally low temperatures
b. side reactions with ozone
c. Difficulty of splitting of the ozonide
d. Explosibility of the ozonide
e. Difficulty of recovery of the end product.

D. Practice

In the carrying out of this invention the following technique is used:

1. The ~~ester or~~ ester derivative of the acetylenic alcohol or glycol is dissolved in a solvent (inert to ozone) to form a 5 to 10% solution.

2. An equal volume of a water slurry containing a sufficient amount of $CaCO_3$ or $Ca(OH)_2$ so as to always maintain neutral or slightly alkaline conditions is added.

3. The ozonolysis is carried out at a temperature range of 2 to 30°C but usually about 10°C with cooling where necessary.

4. An ozone concentration of 2 to 8% by volume in the inlet gas is used; employing conventional gas distribution equipment, the absorption of ozone is quantitative and complete.

5. During the course of the ozonolysis the water and solvent phases and the $CaCO_3$ or $Ca(OH)_2$ are intimately

by the fingers of the gas distribution and the ozonide is decomposed as fast as it is formed and the calcium salt of the acid is formed.

6. only the theoretical amount of ozone is used and at the conclusion of the ozonolysis the water layer containing ~~two~~ a portion part of the Ca salt ~~was~~ is soluble is separated and the remaining Ca-α-~~acetoxy~~ acetoxy ~~succinate~~ aliphatic acid is diluted and ~~added to~~ the two ~~a~~ water solns are combined

7. The free acid is obtained by acidifying the water soln of the Ca salt with H_2SO_4 and then extracting the acid with Et_2O. The solvent is stripped to recover the α-~~acetoxy~~ acetoxy ~~succinic~~ aliphatic acid.

~~In many~~ instances it is advantageous to ~~dry~~ omit the treatment of the Ca salt with a mineral acid to free the α-acetoxy aliphatic acid, and in such cases it is within the scope of this invention to use only water for the hydrolysis of the ozonide. Here again, the water is intimately distributed throughout the solvent phase during the ozonolysis and at the end of the reaction a water soln of the α-acetoxy aliphatic acid is obtained. ~~absorbed~~

[illegible] of the α-acetoxy aliphatic acids as compared with α-OH aliphatic acids, it is

In general, and particularly because of the relative stability of the α-acetoxy aliphatic acids as compared with the α-OH aliphatic acids, it is a feature of this invention that the following factors

a- concn. of acetic deriv. of acetylene alc. or glycol

b- concn. of O_2 in the inlet gas.

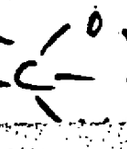
c- temp. of saponifn.

can be varied widely without substantially affecting the yield. These yields range from 95% to quant.

Theor Foundations

Our invention involving the successful synthesis of α-acetoxy aliphatic acids from acetoxy derivatives of acetylene alcs & acetylene glycols via the process of saponifn. hydrolysis rests on these factors

A. In contradistinction to the customary precedents for the triple bond, one acts in a very specific and very definite manner to yield acids. This involves the following steps:

1. The formation of the bridge, structure 

2 pp 3

2. This is followed by the Orlyn of the oxide to yield, at least as intermediate compounds, the diketone plus hydrogen peroxide.

3. action of the hydrogen peroxide on the diketone to give the aliphatic acid

This is a very direct action and as such is far better than the relatively uncertain & many-directional activity of strong oxidizing agents.

B. also, only the theor amt of oxide is needed ~~as a catalyst to~~ while ~~reaction takes place as~~ KMnO4 & K2Cr2O7 require substantial excess

C. The time of reaction is ~~quite~~ very rapid, a ~~factor which makes it a very~~ ~~equipment requirement~~ advantageous trait in all commercial apts

D. The use of the reaction in further reduced ~~by the fact that~~ because there is no necessity for

E. troublesome fill of spent oxidizing agents by ~~the~~ reoxidification of these as well as difficult problems of separating the α-acetoxy aliphatic acid produced.

To sum it up, the action of oxide on the ~~base~~ ~~other~~ derivs of acetylenic alcs ~~is a selective~~ & ~~selective~~

avoids any side reactions & other damaging effects.

V Examples

The following examples serve to illustrate the various methods by which the invention may be carried out.

Example I

22.6 grms (0.1 mol) of 2,5-Dimethyl-2,5-Diacetoxy-hexane-3 are dissolved in 200 cc of CCl_4. To this is added 200 cc of water containing 10.6 grms of Na_2CO_3, ~~is added~~ the carbonate ~~6 times the amount that theoretically~~ & the theoretical amount necessary to combine with (11 grms would be 6.70 in excess) the 2-acetoxy isobutyric acid acid is formed. The mixture was placed in the apparatus described in the corresponding patent application. ~~and operation~~ The operation is carried out at 110°C, allowing only the top layer of ~~oil~~ (11.7 grms = 0.1 mol). ~~The~~

water & solvent vapors are then condensed by passing thru a cooling jacket & distilled back.

~~Results~~
The reaction data are

% by Vol of O_2 in O_2	3.9 %
Rate of flow of feed stock	0.36 liters / hr.
Time of operation	1 hr. 48 min.

At the end of the reaction the Ca-2-acetoxy isobutyrate is present partially in solution in the water phase & partially as a ppt. Sufficient water is added to dissolve all of the Ca salt & the calcium is precipitated by the addition of 62 cc

of 1 gm, HCl (aq). The α-acetoxyisobutyric acid was extracted with Et_2O.

Under cooling & stirring this was given treatment and necessary to neut the ca. ca. $CaSO_4$, ~~and precipitate is checked~~ The work of ~~α-~~

In a continuous liquid-liquid extractor for 48 hrs, 500 cc of an ether solution of α-acetoxyisobutyric acid was obtained. This solution was evaporated first under atmospheric pressure & toward the end under a pressure of 200 mm of Hg to yield 28.3 gm of α-acetoxyisobutyric acid, equivalent to 97 % of theoretical.

Example II (a 0.2 mol)

16.8 gms of 3-methyl-3-acetoxy-butene-1 ~~and~~ dissolved in 200 cc of CCl4 and 200 cc of water containing 11.4 gms of $Ca(OH)_2$ added. The mixture was placed in the reactor ~~oxygenator~~ ~~reactor~~ & oxygenated at 10°C.

The reaction data were:

% by vol of O_2 in O_2	5.3 %
Rate of flow of bubbles	0.22 liter/min
Time of oxygenation	4 hrs. 10 min

~~[illegible]~~ The oxygen passed through in ~~[illegible]~~ ~~the [illegible] to~~ 9.6 gms (a 0.2 mol) this gives the ether and necessary to react with the triple bond. The α-acetoxy ether

Ketopinic acid was recovered & isolated in the manner set forth in Example I, the only variation being that prior to the extn with Et_2O the formic acid (which is also present as a product of the hydrolysis of the oxoacid) was distilled out. The yield of α-acetoxy ketopinic acid was 18.5 gms, equiv to 95% of theor.

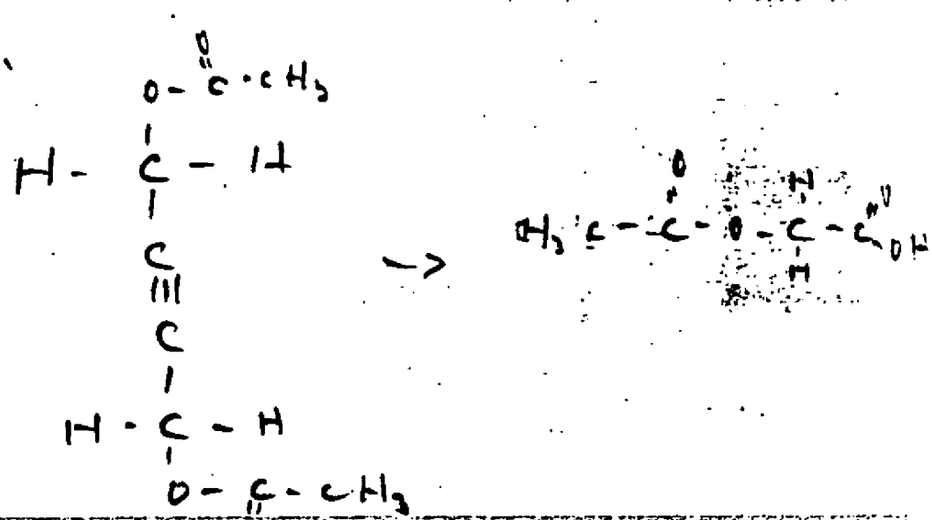
Example III

~~14.6 gms~~ (= 0.1 mol) of 1,4-acetoxy-butene-2 are dissolved in 100 cc of CCl4 ~~and~~ and 100 cc of a saturated solution of CrO_3 in AcOH added. The solution is heated at 110°C. The reaction data are:

~~% by vol of O2 in~~ ~~Cl~~	6.1 %
~~Rate of~~ Rate of flow of mixt, cc/min	0.19 liter/min
Time of operation	2 hrs 6 min

The crude acetoxyacetic acid is treated with H_2SO_4 & ~~the~~ the free acid is extracted & isolated

C	72
O	64
H	10
	146



I claim

1. a process for producing an α-acyloxy aliphatic acid which comprises saponifying a salt of an ester derivative of an acetylenic alcohol & hydrolyzing the saponide formed.

2. a process as defined in claim 1 wherein an inert solvent ~~is used~~ (~~preferably~~) is used as the saponifying solvent.

3. a process for producing an α-acyloxy aliphatic acid which involves saponifying a ~~salt~~ water miscible solvent solution of the ~~ester~~ of acyloxy acetylenic alc. ~~α-acyloxyaliphatic acid~~ in the presence of an equal vol of water containing ~~sufficient~~ the theo amt of alkaline earth carbonate or hydroxide, so as to always maintain neutral or slightly alkaline conditions, & the free α-~~acyloxy~~ acetoxy aliphatic acid is subsequently recovered by treatment of ~~its~~ the alkaline earth salt with a mineral acid, only at the time the formic acid which is also formed, extracting the α-acetoxy aliphatic acid with a solvent, & finally isolating the α-acetoxy aliphatic acid from the solvent solution.

4. a process as defined in claim 3 in which the saponifying is carried out at a temp of 2 to 50°C but usually about 10°C.

5. a process as defined in claim 3 in which

The ester content is in the region of 2 to 9 %, by volume of the mixed gas.

6. A process for producing an α-acyloxy aliphatic acid from the 1,4 diacyloxy derivative of a 1,4-acetylene glycol which comprises saponifying a solution of the 1,4 diacyloxy derivative of the 1,4 acetylene glycol & hydrolyzing the saponifier formed.

7. A process as defined in claim 6 in which an inert solvent (~~[illegible]~~) is used as the saponifying solvent.

8. A process for producing an α-acyloxy aliphatic acid which consists of saponifying a water insoluble solvent soln of the 1,4 diacyloxy derivative of the 1,4-acetylene alcohol in the presence of an equal vol. of water containing the theo. amt of alkali earth carbonate or hydroxide so as to always maintain neutral or slightly alkaline conditions, & the free α-acyloxy aliphatic acid is subsequently recovered by treatment of the alkali earth salt with a mineral acid, and extracting the α-acyloxy aliphatic acid with a solvent & finally isolating the α-acyloxy aliphatic acid from the solvent soln.

9. A process as defined in claim 8 in which the saponification is carried out at a temp of 2 to 50°C but usually at 110°C.

10. A process as defined in claim 8 in

in which the gas comes from the range of 2 to 8%, by volume of the inlet gas.

The process of claim 5 where the said acetoxy ~~acetate~~ derivative of the acetylenic alcohol is 3-~~acetoxy~~ methyl-3-acetoxy-butene-1 and the α-acetoxy aliphatic acid is α-acetoxy-isobutyric acid.

~~11. The process of claim 2 where the said diacetoxy derivative of the 1,4-acetylenic glycol is 2,5-dimethyl-2,5-diacetoxy-~~

12. The process of claim 5 where CuCl is the catalyst solvent.

13. The process of claim 5 where $CuCl_2$ ~~or Cu(OH)₂~~ or the alkali earth carbonate

~~14. The process of claim 5 where sulfuric acid~~

15. The process of claim 5 where the said 1,4-diacetoxy derivative of the 1,4-acetylenic glycol is 2,5-dimethyl-2,5-diacetoxy-~~[illegible]~~ hexene-3 and the α-acetoxy aliphatic acid is α-acetoxy isobutyric acid.

The oxidation of acetylenic alcohols and glycols

1. Statement of Invention — This invention relates to a process for the oxidation of acetylenic alcohols or glycols to produce the corresponding alpha-hydroxy aliphatic acids; more specifically it concerns the production of alpha hydroxy aliphatic acids from acetylenic alcohols employing O_2 as a means of introducing oxygen into the molecule.

The α-hydroxy acids obtained are valuable as intermediate materials in organic syntheses. Especial reference is had to the use of these acids as in the procedure for the manufacture of acrylic esters as described in co-pending patent application —

2. Prior art — Some attempts at oxidation of acetylenic alcohols and in particular acetylenic glycols have been made using conventional oxidizing agents but these have

all led to either low yields or to complete failure. Thus

a. J. Du Pont used $KMnO_4$ (in 70% H_2SO_4) at low temp but the obtained very poor yields and the product for the most part consisted of acetone and oxalic acid.

on ozonolysis yields

anticipated Diol

b. V.N. Ivanov, A.E. Akopyan and S.E. Polyakova tried the action of (1) ~~conc HNO3 & dil HNO3~~

Reagent	Reaction & yield
(1) conc HNO_3	low fractions & no products
(2) dil HNO_3	No yield NO_2 compds
(3) K.Cr.O7 in H_2SO_4	70-80% of ~~[illegible]~~ acetic acid and minimally MeEtCO (1)
(4) 50% H_2SO_4 in presence of $FeSO_4$	60-70% of
(5) $KMnO_4$	no products can be isolated

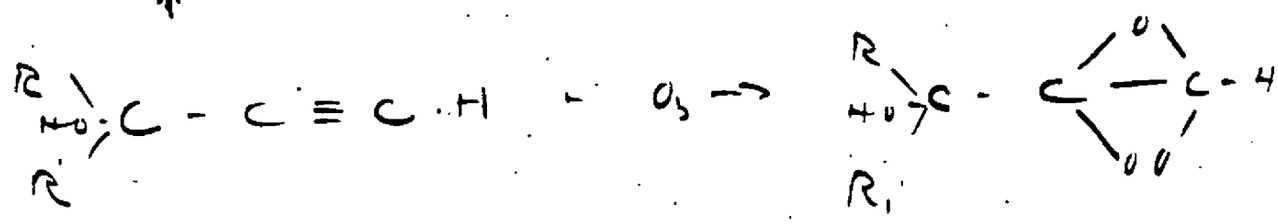
c. Critique - While the desired problem of the oxidation of the C=C to yield ~~[illegible]~~ the corresponding diols ~~[illegible]~~ in presented as being ~~[illegible]~~ practical. There are many pros & cons of such an unusual oxidation

x/ — and they are principally confined to to simple HC ~~[illegible]~~ acetylenic compounds [illegible] 0 bearing radicals. Thus acetylene ~~[illegible]~~ has been oxidized to oxalic acid using HNO_3 +

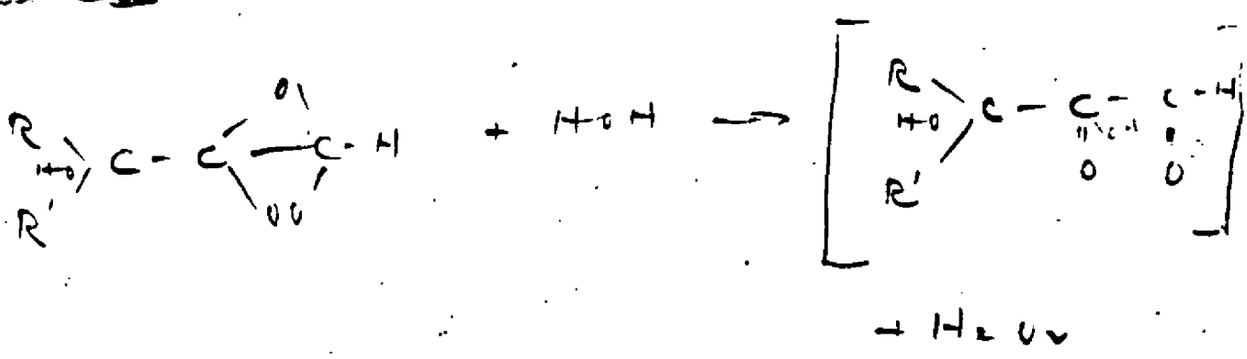
In the case of acetylenic compds ~~[illegible]~~ having OH groups in their structure, the labiality of ~~both~~ the OH both before & after the action of the oxidizing agent ~~[illegible]~~ gives rise to the poor yields obtained in the cited prior art. It is admitted by both Dupont & L'avon (and co-workers) ~~[illegible]~~ that ~~[illegible]~~ the react. proceeds through the formation of the a-OH acid but that this is readily labile ~~[illegible]~~ ~~(particularly [illegible]~~ & is further oxidized to acetone + CO_2. particularly is this shown in the case of ~~[illegible]~~ $KMnO_4$, $K_2Cr_2O_7$ & H_2O_2-$FeSO_4$ would demolish the ([illegible] fail to appear [illegible] up of the molecule [illegible] as formed [illegible]) also for HNO_3 the use of the conc acid results in so vigorous & destructive an action that ~~the~~ drastic decomposition occurs while the dil acid causes the acid to act as nitrating [illegible] the ~~[illegible]~~ principal product being an nitr[illegible] [illegible] are dependent on finding an oxidizing

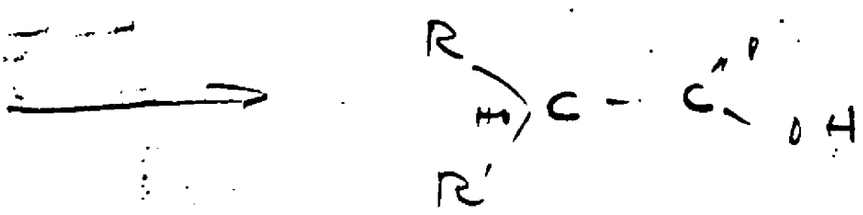
Novelty - A general conversion is based on the fact that acetylenic alcohols & glycols will react, about O_3 to yield an ozonide. This ozonide can then be split by the action of water to yield the corresponding dicarbonyl α-OH acids.

Thus, in the case of an acetylenic alc.



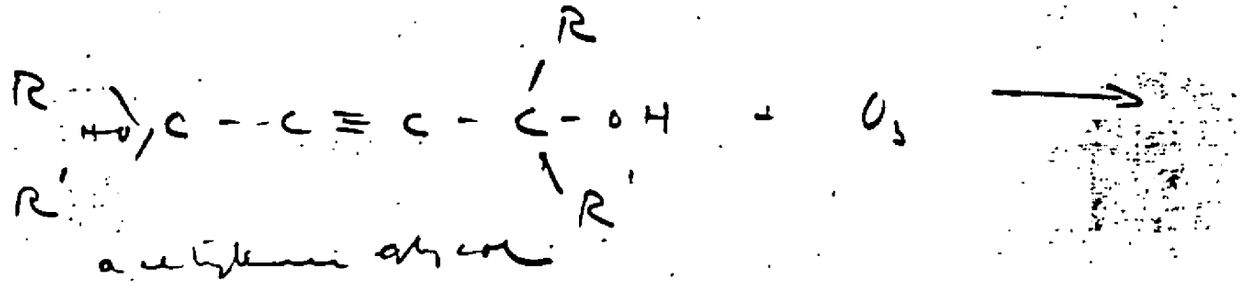
Then



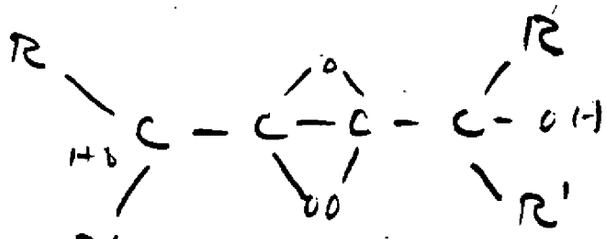


where R and R' may be the same or diff alkyl radicals

B. For an acetylenic glycol O

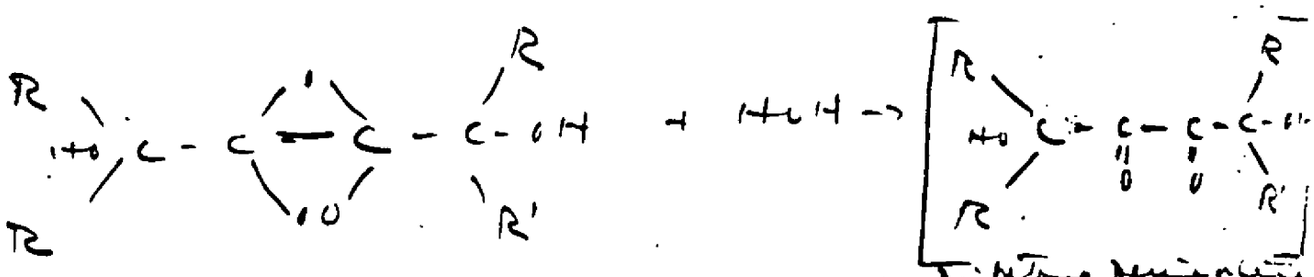


acetylenic glycol

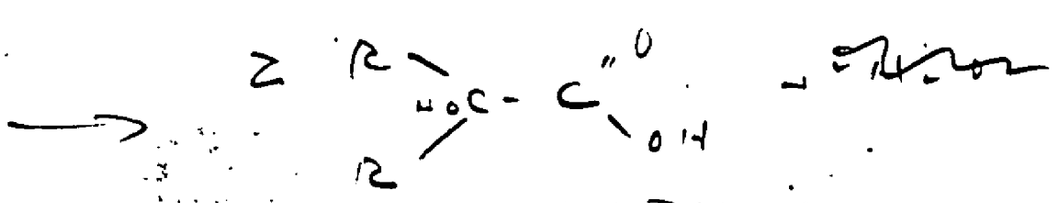


monoxide of acetylenic glycol

then



α-diketone glycol + H₂O



α-OH dihydroxic acid

So far as we are aware, there are no instances of the use of O_3 to transform acetylenic alcohols & glycols to α-OH dihydroxic acids also and believe this to be the first

B. ~~Practice~~ (O) ~~[illegible]~~ is thus fr
commercially feasible method ~~[illegible]~~ the production of a ~~[illegible]~~ the organic chem
~~[illegible]~~ but the organization of the C-C.
This is due in part to the high yield obtained
& in part to the low need for special precautions usually
employed in organization reactions such
as,

a. abnormally low temp.
b. side reactions with O_3.
c. difficulty of splitting of ozonide.
d. explosibility of ozonide.
e. difficulty of recovery of end products.

B. Practice — The acetylene or other volatile (gas) is dissolved in acetone or dilute HOH to form a ~~[illegible]~~ 5-10% soln. but the ozone
$Ca(OH)_2$ is added to ~~[illegible]~~
The ozonolysis is carried out at ~~[illegible]~~
The quick ~~[illegible]~~ the pressures range ~~[illegible]~~ of
2-30°C with cooling where necessary. Ozone
to a conc. of 2-8% in the inlet gas
is used; ~~[illegible]~~ conventional ozone
distribution & the absence of O_2
[illegible] the case where water

is employed the oxyacids decomposes as readily as formic (particularly in the presence of $Ca(OH)_2$ or $CaCO_3$) and the carbon of the acid is reduced directly. + denitrification. This is subsequently recovered by careful neutralization of the carbonate with H_2SO_4 & extraction of the acid (or) mixture of transuranic in the form of oxyacids a solution (~~[illegible]~~) ~~[illegible]~~ the decomposition is carried out by the addition of ~~[illegible]~~ containing $CaCO_3$ in which

—4—

IV The foundations

While the addition of two substitutes to the organic chemistry has been known for ~~[illegible]~~ about 100 years, anything approaching quantitative method has only ~~[illegible]~~ been put on a firm basis in the last 50 years. ~~[illegible]~~ beginning principally with the work of Harries in Germany from 1914 and of ~~[illegible]~~ only in the case of Kunckell & Sontgerath with ~~[illegible]~~ various investigations in the U.S. such as Hurd & Christy, Jacobs, Stevenson ~~[illegible]~~ in any recent years, has the reaction been established on anything like an approaching a quantitative. ~~[illegible]~~

~~The theoretical basis for the mechanism follows~~

~~The theoretical basis for the~~ involving the interpretation of mechanism

This invention has its foundation in the ~~in the~~ ~~following facts~~ facts:

A. Ozone preferentially attacks unsaturated linkages in a cpd before ~~any attack begins on other~~ ~~in the~~ OH groups (or other carbon of ozonolysis) ~~This~~ only when the unsaturated linkages have been completely reacted is there any possibility of attack on the rest of the molecule.

B. Further, in the case of ~~unsaturated~~ olefinic alcohols, ~~no attack~~ be they primary, secondary or tertiary, no attack whatever takes place on the OH group & only the amt of O_3 is absorbed which is necessary to ozonize the dble bond.

A. Ozone in contradistinction to conventional oxidizing agents for the trifle bond acts in a specific and very set manner to yield ~~products~~. This manner involves the following steps

(1) The preparation of the ozonide

(2) Hydrolysis of the ozonide to yield, ~~etc~~ (as well as an intermediate compd) the diketone plus H_2O_2.

(3) action of the H_2O_2 on the diketone to yield ~~[illegible]~~ adipic acid.

This is a very ~~[illegible]~~ direct action & as such is fine material to ~~[illegible]~~ & certainly an interesting activity of strong oxidizing agents.

Particularly ~~[illegible]~~ such a new ~~[illegible]~~ reaction presents an sure & clean cut method for converting acetylenic alcs & glycols to α-β-γ acids ~~by utilizing~~ ~~[illegible]~~ utilizing the selective action of O_3 on the triple bond ~~[illegible]~~ & avoiding any side reactions ~~[illegible]~~ ~~[illegible]~~ or other deleterious effects. It should especially be noted that ~~[illegible]~~ ~~[illegible]~~ ~~[illegible]~~ in choosing O_3 we have selected one agent to which the final product of the reaction is ~~[illegible]~~.

Examples I - (the following) examples serve to illustrate the various methods by which the invention may be carried out

Example I: 14.2 grams of (0.1 mol) 2, 4-Dimethyl-2, 4 Dihydroxy-Hexane-3 are dissolved in 200 cc of water and placed in the chamber A of the apparatus shown (Fig 1). Oxygen gas is passed first through the water scrubbing bottle B to remove traces of H_2S and then through the fritted glass gas distributor C. This latter is very fine and an excellent gas distribution is obtained, the level in the apparatus rising from 2 to 3 feet. The oxidation is carried out at 10°C and the gas and liquid thoroughly mixed (ca. 5°/hr) controlled by the circulation of 5°C water in the cooling jacket. The oxidation is complete in 5 hrs with the absorption of the exactly theoretical amount of oxygen. (= 4.8 grams O_2) = 0.1 mol

For the separation of the 2-oxo-1H-B-acid the following technique was used

2 ~~cc~~ 36 ~~cc~~ cc of ~

1070

solution was finally added to the original filtrate. The ~~CaCO3~~ Ca as $CaSO_4$. This is quite the thing and well dense. The precipitate is filtered off & the solution of α-OH I.B. acid extracted with Et_2O in a continuous liq.-liq. extr. for 4 hrs. After a 500 ml of Et_2O soln was obtained. This was the second fract. under atm. & the under vac → 19.6 gms = 92% of theor. of α-OH I.B. acid.

air H_2O_2 → calcd → slowly.

Example II 105 gms of Diol (1st mole) was shaken in ~~[illegible]~~ 700 ml. water & oxidized at 10°C in the manner described in Example I. The data are:

% O2 in O2	4.2%
rate of flow	0.5 liter/min.
Time	4 hrs.
~~Temp~~	~~10°C~~

The α-OH acid was extracted with Et_2O and the extract worked →

as the oxidation proceeded the ~~[illegible]~~ ~~[illegible]~~ ~~[illegible]~~ more Diol in the reaction than the diacid

(13)

Example 3. (~~16.8~~ 8.4 grams of ~~MgO~~ 3-Mg - 3-β H-Butyrate (or calcium salt) are dissolved in 200 cm of water and oxygenated at 10°C in the apparatus described.

% Oxygen O_2	12.6 %
Rate of Flow	0.5 liter / min.
Time	

claims. I claim: O

1. a process for producing an α-OH aliphatic acids from an acetylenic alcohol which involves the splitting of the triple bond under the action of O_2 to yield the carboxyl group.

2. a process for producing 2 moles of α-OH aliphatic acids from 1 mole of

89

9D

11D

11D

11D

11 hrs

4 hrs

4.6 amb / hrs

9.

The invention relates to a novel process for the production of monomeric acrylic esters.

The steps involved are

A. Reaction of an aldehyde or ketone and HCN to form an acrylonitrile or alpha-substituted acrylonitrile.

B. Saponification or esterification of the OH group (or groups) on the acrylonitrile alcohol or glycol followed by esterification of the ~~other~~ ~~acid~~ alcohol of the acrylonitrile alcohol or glycol to yield an alpha-ether or ester aliphatic acid.

C. Esterification of the carboxyl group ~~the alpha ether~~ ester aliphatic acid by a monohydric alcohol to form an ester of ~~the alpha ether~~ ester aliphatic acid. This is followed by the pyrolytic splitting of the ~~alpha ether~~ ester of the aliphatic acid to form the monomeric acrylic ester.

[illegible]

A [illegible]

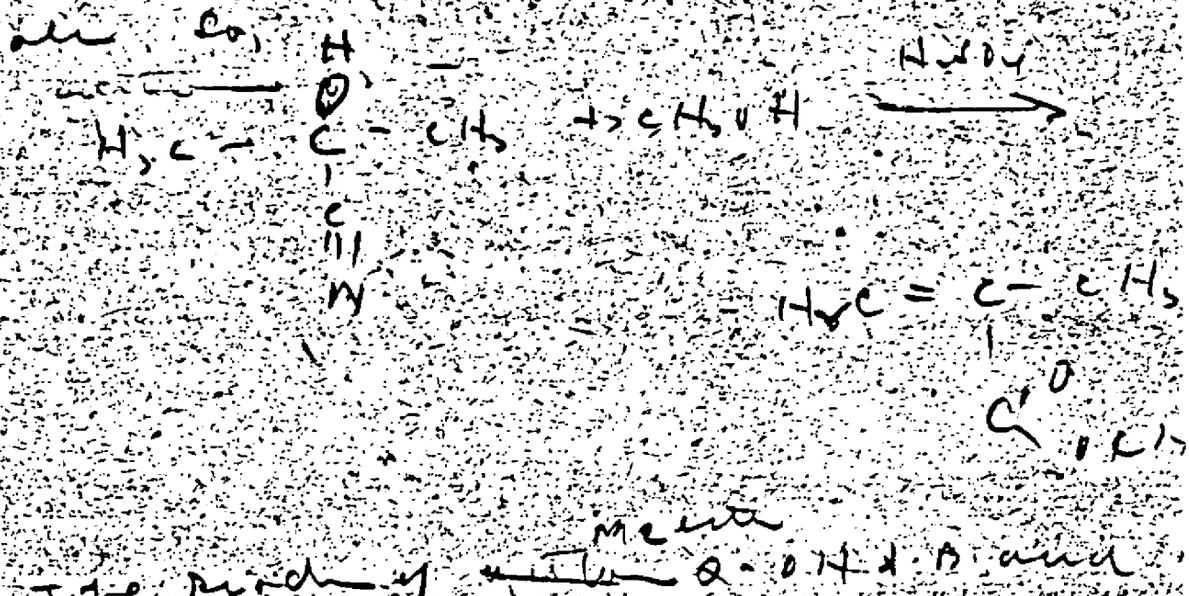
[illegible]

[illegible]

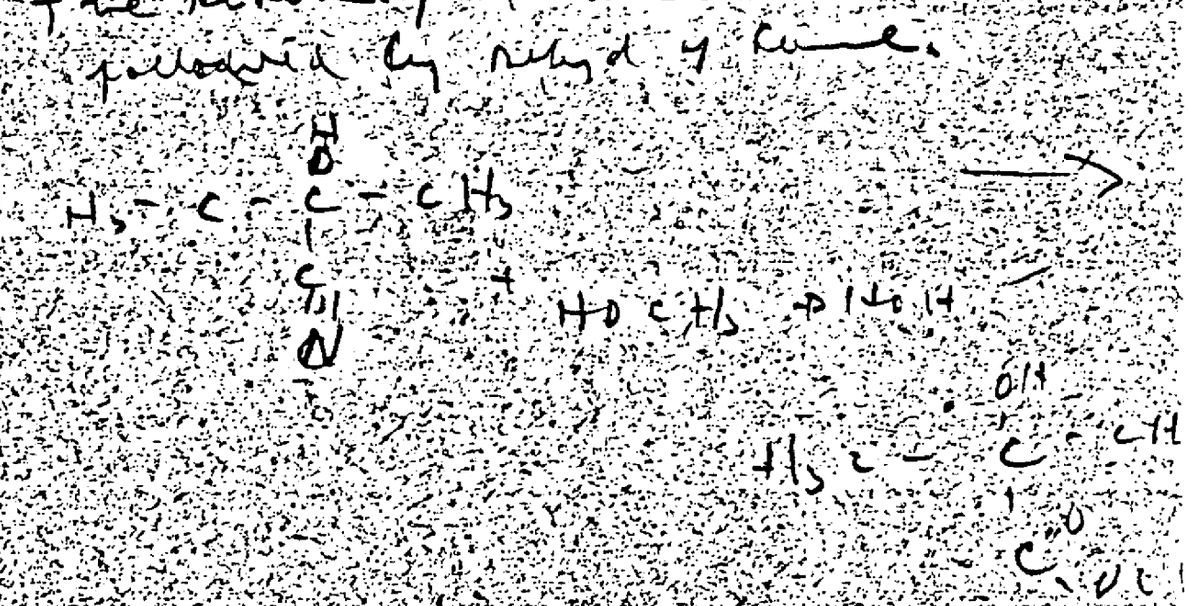
[illegible]

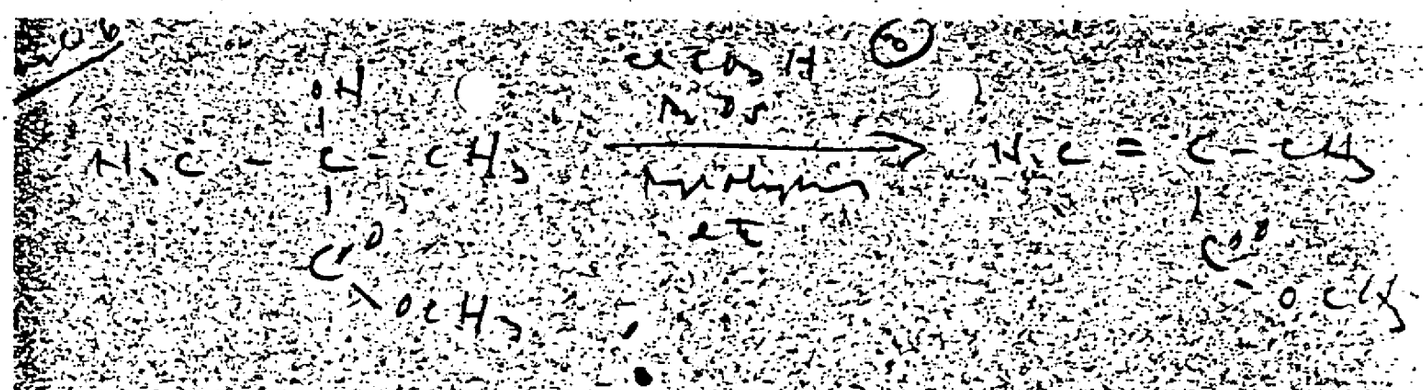
[illegible]

[illegible]



The [illegible] of [illegible] Q. O.H. & B. and followed by [illegible] of [illegible].





Critique

All of the above methods suffer from the usual faults

1. The HCN & NaCN used in the formation of the cyanohydrin is according to some & doubtful the chemical model either a dot or commercial model. This since either answers equally well to the product formed. Finally the last method is very time & labor consuming & requires repeating & careful control handling.

2. In all methods the direct conversion of the hydroxy to nitrile there is a time double bonding for both the cyanohydrin & the methoxy compounds formed from it to polymerize during the work. This is important. The ~~[illegible]~~ yields of around 75%.

3. The use of NaCN or HCN are relatively dangerous & are not reading available

[illegible]

II. Notation

A. Stoichiometry

The stoichiometric coefficients can best be illustrated by the following equation. We should use MeMe as an example.

1. Production of kind [illegible] kind followed by [illegible] of kind

2. Extrapolating of [illegible] & [illegible] other [illegible] of kind [illegible] by [illegible] of [illegible]

F. [illegible] We have accomplished all that of the above in which [illegible] from 9 v 9 up to nearly pure [illegible] or pure [illegible], then we have [illegible] the list of [illegible] of MeMe [illegible] the route. F. [illegible] our methods have [illegible] of the [illegible] [illegible] unique & [illegible] described fully in [illegible] [illegible]

application

[illegible] the [illegible] [illegible] the [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible]

[illegible]

[illegible]

a. [illegible] KOH [illegible]

b. [illegible] NH [illegible]

c. add ketone

d. react [illegible] @ [illegible]

e. hydrolysis at 0°C

f. [illegible] of [illegible]

g. [illegible] → [illegible]

h. purification of α-acylated alkylation

and

a. acidification of OH group [illegible]

b. [illegible] solvent [illegible]

[illegible]

c. addition of equal volume of [illegible]

cooling to [illegible]

always [illegible]

condition

d. [illegible] at [illegible] 10°

followed by [illegible] of α-acyl

dehydration →

e. alkylation and

[illegible] of α-acyl alkylation and by

f. heating with [illegible] or H_2CO_4

followed by [illegible] of α-acyl alkylation

and

g. [illegible] of [illegible] acyl [illegible]

[illegible]

[illegible]

[illegible]

Regarding the above outlined technique the following should be noted:

(1) The [illegible] autoxidation of [illegible] should be carried out [illegible] from any [illegible] or adding [illegible] but [illegible] autoxidation is [illegible] because it leads to the formation of [illegible]

(2) The CH_3OH formed on the [illegible] can be activated albeit more slowly by the use of $AlCl_3$ + toluene, distilling azeotropically [illegible] $AlCl_3$ or its [illegible] or mixtures of water containing a [illegible]

(3) [illegible] of the [illegible] autoxidation [illegible] the use of CH_3OH [illegible] of the [illegible] of [illegible] [illegible]

(4) The [illegible] [illegible] the [illegible] [illegible] [illegible] [illegible]

[illegible] is based on these 5 main facts

A The reaction in the [illegible] [illegible] the initial formation of [illegible] and the [illegible] & ~~[illegible]~~ relatively easy use of HCN & NaCN & [illegible] with C_6H_5 [illegible] [illegible] ~~[illegible]~~ & [illegible] the [illegible] KOH as we have ~~[illegible]~~ shown ~~in~~ in Co-patent application. The [illegible] proceeds smoothly & readily & in almost quantitative yield. Also the ~~[illegible]~~ [illegible] is in effect ~~[illegible]~~ is not poisonous & requires no special care in stabilization

C The [illegible] ~~of the~~ ~~[illegible]~~ of the [illegible] gives a sure & clean method for producing in very high yield [illegible] & [illegible] [illegible] ester. ~~The~~ [illegible] The [illegible] [illegible] been described in patent [illegible]

B The [illegible] of the [illegible] in a [illegible] & [illegible] [illegible] [illegible] [illegible] [illegible] acids in two ~~[illegible]~~

D The [illegible] of ~~[illegible]~~ [illegible] two [illegible] [illegible] known in the art [illegible] a [illegible] [illegible] [illegible] [illegible] comment [illegible] & [illegible] [illegible]

E The properties of the ~~[illegible]~~

Thus it can be seen that a [illegible] [illegible] [illegible] all of which [illegible] readily carried out steps ~~[illegible]~~ ~~[illegible]~~ obtained in high yields.

[illegible]

a. [illegible] of [illegible] [illegible]

b. [illegible]

c. [illegible] of [illegible] [illegible] [illegible] [illegible] [illegible]

X. Examples

Example I.

a. [illegible] of KOH (85%) + [illegible] are added to [illegible] of benzene (mp. 120°C) [illegible] and [illegible] equipped with a stirrer, a reflux condenser.

b. The mixture is heated to 120°C with the [illegible] and KOH liquefies [illegible] and becomes uniformly [illegible] distributed throughout the benzene.

c. The mixture, the benzene, 75 grams of [illegible] 80% calc. (10% excess of the [illegible]) to combine with the water [illegible] the KO [illegible] are added at [illegible] 120°C [illegible] for [illegible] to [illegible] completion of the [illegible]. The mixture consists of an [illegible] of very finely divided KOH plus [illegible] and a relatively small [illegible] of the [illegible]

[illegible] adequate precautions to prevent an explosion with liquid air. The flask is thoroughly washed with dry ether & dried first in [illegible] filter & then is a short time under [illegible]

f. The dry CO_2 is stirred into a mixture of pure methyl ester with ether & is placed ~~[illegible]~~ in a reactor ~~[illegible]~~ of assembly consisting of

(1) a tightly fitting lead,
(2) a gas dispersion tube, coarse grade,
(3) an efficient agitator,
(4) a thermometer,
(5) a gas funnel for adding the alcohol,
(6) a gas exit tube.

g. Ethanol is purified for 3 [illegible] or 5 [illegible] to [illegible].

h. The [illegible] is allowed to rise to 13-15° and 57 gms of dry alcohol are [illegible] very rapidly & a very vigorous acid [illegible] ~~[illegible]~~ maintained.

i. After 25 [illegible] a very sharp heat rise takes place & the [illegible] rises to a very pasty consistency. The temp ~~[illegible]~~ is kept at 13-15°.

j. The agitator is stopped & the reaction is allowed to continue for 2 hr.

k. The mass is cooled to 0°C & hydrolyzed with 200 gms of chopped ice to which two drops of methyl red & dil acid are added. The bottom layer the ~~[illegible]~~ co (14) ✓

[illegible]

The R mixture (the large is diluted & treated in a small amt of solid KOH. The ether is distilled 10 times with some portion of methylal (with the small portion of solid KOH being added to aid the removal of the methylal). & the methylal ests are added to the main bulk.

The combined methylal ests are washed twice with some portion of sat salt soln. The pH is now 8.

The ester is distilled first at 1 atm. pressure and then under vac to strip off the last methylal. The yields are

54 gm prod

12 gm methyl

98% on acetic ~~started~~ charged.

The product is returned to process for the next run & low-ter

~~Exp 2~~

Exp 2

1.4 gm of prod are treated with

[illegible] mg of α-ketoglutaric dissolved in [illegible] cc of [illegible] an equal vol of [illegible] water is added to [illegible] and [illegible] cc so as to always [illegible] [illegible] with [illegible] conditions. The mixture is placed in the syringe described in the corresponding patent and the syringe is mounted on a [illegible] [illegible] the [illegible] of [illegible]

The Data are

Vol of [illegible]	[illegible]
Rate of flow of [illegible]	0.50 liters/min
Time of [illegible]	[illegible] 50 min

The [illegible] of [illegible] is [illegible] by water & [illegible] to the α-ketoglutaric solution. The [illegible] and [illegible] is [illegible] [illegible] & [illegible] in [illegible] [illegible] [illegible] the NaH [illegible] & [illegible] [illegible] [illegible] α-ketoglutaric [illegible] [illegible] & the [illegible] [illegible] [illegible] to [illegible] the free acid. The [illegible] is [illegible] with a [illegible] [illegible] to [illegible] the acid.

[illegible] α-ketoglutaric acid [illegible] mg of α-ketoglutaric acid [illegible] added 12.8 mg [illegible] 0.5 mg of

65-4307

Ex 12 H

Seminar 1 ① 12-12-46

I Chemistry { 1 Inorganic (Sem 1)
2 Organic
3 Physical

II Chem. Eng { 2 Lectures

III Mech. Eng { 2 Lectures

IV Elect. Eng { 2 Lectures
Instrumentation

V Structural Eng.

Lecture

a. Texts & complete outline of lectures.
b. Examples from actual work
c. Discussion of problems [illegible]
d. 1½-2 hrs. for lect.
1½ hrs for questions, illustrative examples, etc.

[illegible] office (2) 12-12-46

Ratio H transfer surfaces
Water mains

Life of Plant

2. Y main coordinate of chem.

Temp. } Reproduce these
Press. } conditions
Conc. }
Time }

appreciation of corrosion problems.

1. Special Considerations — Reliability, etc.

Elect. Eng.

1. Instrumentation for control

2. Telemetry

3. Agitation by Ultrasonic Waves

4. Induction Heating of Vessels

Chemical design

Organic catalysis

Inorganic — [illegible]

---

(3) 12-12-46

Lecture Review Questions to
Lecture and Points

Chem

1. Chem change or physical change
— really can't differentiate
a - understanding of atomic structure
2. Can't divorce from matt.

$x \overline{P_1} = P$ Boyle's law
and
partial pressure

3. Prog — paper headache — lack of time
of experience

4. Structure of atom
5. atomic No. & atomic wt.
6. Nature of chemical combination
: loss or gain of electrons
transfer.
7. Concept of Valence.

Dean S. Edmonds
Frank E. Barrows
W. Brown Morton
Merton W. Sage
Willis H. Taylor, Jr.
Raymond F. Adams
R. Morton Adams
Ernest H. Merchant
George E. Middleton
Morris D. Jackson
Leslie B. Young
Daniel V. Mahoney
Donal F. McCarthy
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W. B. Morton, Jr.
Arnold R. Workman
John Bodstead

February 21, 1947

13,610

Mr. Abraham Brothman
A. Brothman & Associates
2928 - 41 Avenue
Long Island City 1, New York

Dear Mr. Brothman:

In our recent examination of your patent data relating to the process of manufacturing methyl methacrylate monomer, we particularly called your attention to four patents which we regarded as of considerable importance with respect to your process steps.

We find that in the Patent Office proceedings the following references, as listed, were cited with respect to each patent:

Patent 2,054,242, Cocker et al

References	1,942,577, Siebenberger Br. 377,249

Patent 2,163,720, Vaughn

References	1,169,341, Merling Ger. 280,226

Patent 2,385,546, Smith

References	2,161,191, Perkins 2,163,720, Vaughn 2,250,445, Bruson et al 2,326,099, Kokatnur et al 2,345,170, Zeltner et al

Patent 2,385,547, Smith

References

2,130,525, Coleman et al
2,161,191, Perkins
2,163,720, Vaughn
2,248,019, Frieser et al
2,250,445, Bruson et al
2,345,170, Zeltner et al

Sherman "Organic Analysis", 2nd Ed., p. 145 (Div.6)

You will note that the Russian literature citations were not used against the Vaughn patent.

Some of these references seem to be of considerable importance, and possibly your Mr. Gold will have a chance to examine them at the public library. Your attention is particularly directed to Nos. 2,161,191; 2,250,445; and 2,345,170. The data in the Official Gazette with respect to the last-mentioned patent is as follows:

"Patent No. 2,345,170, Process of Making Acetylenic Carbinols
Joseph Zeltner and Michailas Genas, Paris, France; vested in the Alien Property Custodian. Application March 29, 1940, Ser. No. 326,804. In France June 16, 1939
(Cl. 260--638)

1. The process of manufacturing an acetylenic carbinol by reacting acetylene with a member of the group consisting of aliphatic aldehydes and ketones in the presence of solid potassium hydroxide in a solvent medium including, the step of effecting the reaction in an acetal as a solvent."

This claim would apparently be infringed by the first step of your process.

Copies of the three patents referred to above were ordered.

Yours very truly,

Arnold R. Workman

C O

AMERICAN CYANAMID COMPANY

30 ROCKEFELLER PLAZA
NEW YORK 20, N.Y.

CABLE ADDRESS LIMENITRO

TELEPHONE CIRCLE 7-0100

January 7, 1947.

A. Brothman & Associates,
8503 - 57th Ave.,
Elmhurst, L. I.

Attention of Mr. A. Brothman.

Gentlemen:

Mr. C. P. Davis of our Technical Division advises of your interest in Ammonium Metavanadate and in accordance with your request, we are making a five pound shipment from our Bridgeville, Pa. plant.

This material is available in limited quantities from time to time at the following prices:

$2.40 per pound in 100 pound or more lots
$2.50 per pound in 25 pound lots
$2.75 per pound in less than 25 pound lots.

These prices are f.o.b. Bridgeville, Pa. and the usual terms are net thirty days.

If there is any additional information which you feel we can supply, please do not hesitate to write to us again.

Very truly yours,

AMERICAN CYANAMID COMPANY

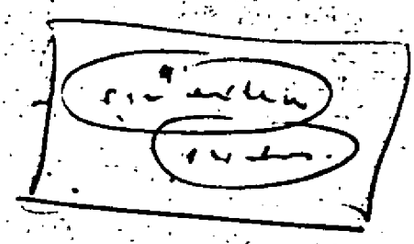
E. J. Tuthill

E. J. Tuthill,
Synthetic Organic Chemicals Dept.

dc

[illegible]

300 [illegible]
[illegible] CB.
1000 [illegible]



300
[illegible]
1600

1300

65-4307-1-B-7

65-4307

Ex 1/2 II

1. polymer in higher ketone solvent — then strain
distill ketone.

2.

Crude

1. get n. polymer in 1+0
2. add amount beyond amount to date — 119/900 gal
3. mix 6 hrs.
4. Look for increase in turbidity & viscosity of soln.
5. Take one portion & add NaCl to salt up polymer & drain out
6. If drains out — filter or centrif. or distill
   see if can work salt out & if can redissolve polymer in 1+0.

---

1. prep a 1 pct a powder using normal techniques.
2. Take one portion at 1 hr.
   " " " 4 hrs
   " " " 8 hrs
   " " " all day
   } Study gel time in color

---

3. prep another batch
   work 0 x
   ✓ x
   5 x
   10 x
   Send all filtrates

13.61
11.50
V.11
13.61

Take RQH powder & slurry in 49/800 gal mix

49.25
49.01
11.50

remove at end of 1 hr & 6 hrs.

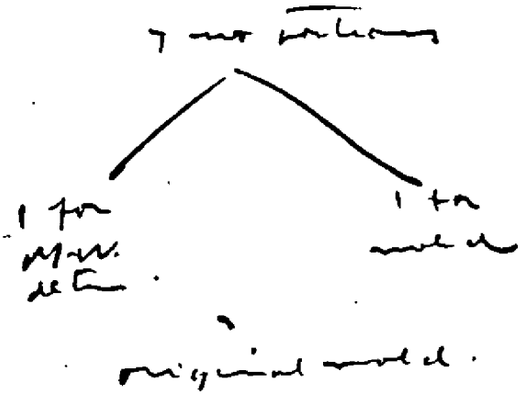
[illegible] cat. in 1+0

particle shape –

Higher M.P stuff in separating powder

Take R & H 9 do separating.

our distrib of M.W. may be diff.



1. Surface Theory

K & H among

~ actual polymer. enters after polym

by extended time of contact with [illegible]

3. Polymeric [illegible]

3. chain interrupts [illegible] polymer

4. [illegible] polymeric [illegible] method off

with H₂O.

5. [illegible]

6 M.W. Intro G. by measures K & H.

Diethylene glycol monolaurate

Stearic

1 free OH

low H-O solubility

if do not add glycol

dissolve the acid

polyethylene glycol

monolaurate

or

use high amount of polyethylene

glycol monolaurate

glycol monostearate

S 9 v 8

4 g

Sample bottle full = 346.6 gms.
Filter " empty = 225.3 "
Sample " " = 247.0 "
Filter " full = 323.2 "

323.2
225.3
97.9

346.6
247.0
49.6
97.9
2.7

Sample bottle empty = 244.6
" " full = 261.0
" " evaporated = ~~258.8~~ 252.1

261.0
244.6
16.4
~~16.2~~ 7.5
~~0.2~~ 8.9

252.1
~~258.8~~
244.6
~~14.2~~
7.5

fat/gmer = .05 (16.4)

$$\% = \frac{.05(16.4)}{\cancel{16.2}\ 7.5} = 11\%$$

9.
8.72
.28

25
24 × 2.5
3

10
10 + 30

---

40 25 ~~50~~ 25 10

10-1-46

Program for MeMe Powder Work

I. Removal of adhered(?) Gum arabic Film

A. assemble various recently prepared (within the last week) batches of powder and slurry these with 5-10 times the wt. of 1% NaOH, the caustic soln. to be at 60°C. Then:

1. Filter the powder.
2. Wash the powder 5 times (with filtration each time) using water at 85°C.
3. Dry the powder at 90°C. for 16 hrs. and mold.

B. Prepare a fresh batch of MeMe powder using the "normal" proportions of:

100 gms. monomer
2 gms. Benzoyl Peroxide
4 gms. Gum arabic
700 gms. Water

Repeat the NaOH washing as in "A".

I. Use of Emulsifying agents requiring smaller amounts than Gum arabic

A. Prepare a series of powders using

100 gms. Monomer
2 gms. Benzoyl Peroxide
0.25, 0.5, 1.0 & 2.0 gms. Agar
800 gms. Water

10-1-46

I: Use of Diallyl Phthalate Polymer as a Dispersing agent -

A - Try to prepare a powder using the already prepared Tacky material resulting from the use of 2% Benzoyl Peroxide. Thus, use:

100 gms. monomer
2 gms. Benzoyl Peroxide
0.5, 1.0, 2.0, & 4.0 gms. Diallyl Phthalate Polymer
800 gms. water

B - If powders result from any of the above, repeat using 1% Benzoyl Peroxide.

V. Emulsification in an alkaline medium

A. adjust the pH of a gum arabic soln. (4 gms./800 gms. H_2O) to 8 with NH_4OH. Heat to 80°C and add the MeMa monomer. Check the pH and if it has dropped below 7.5 adjust it to 7.5 - 8.0 with NH_4OH. Carry out the polymerization in the usual manner.

B - Repeat "A" using the minimum amount of agar (as determined in "II, A") which will give a powder.

Note - In "I, A", first check the solubility of gum arabic in 1% NaOH.

Polymerization of Vinyl Derivatives in Suspension

W. P. Hohenstein,
F. Vingiello, and H. Mark
Polytechnic Institute of Brooklyn

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Polymerization of Vinyl Derivatives in Suspension—I

W. P. Hohenstein,[1] F. Vingiello,[1] and H. Mark[1]

IN THE last few years several authors (1-20)[2] have succeeded in elucidating the mechanism of the polymerization of ethylene derivatives in the homogeneous liquid phase (either in bulk or in solution) to a considerable extent. It seems that the total reaction consists of several steps, which are chemically very distinct from each other, but take place simultaneously or in quick succession during the course of the polymerization (21-32).

There is first the *activation*. It can be effected by the action of heat or light or preferably with the aid of a catalyst (2, 3, 14, 16, 31-37). It should be mentioned here that it seems to be more appropriate to speak of an initiator or, still better, of an *initiating complex*, because there is much evidence for the fact that in many cases the so-called catalyst is consumed by the reaction, and fragments of it appear in the final polymer. In most practical cases, mainly revealed in the recent patent literature, one does not use a single initiator such as a peroxide, ozonide, or metal halide, but uses an initiating system, usually consisting of an oxidizing and a reducing agent. Both collaborate in producing the activated polymerization nuclei and maintain (at least over a certain period) a stationary concentration of them.

The next distinct step is the *propagation* or growth of the chains, which may consist in the simple rapid addition of monomer to the activated nucleus (3, 12, 16, 27, 33-38) or, in more complicated cases, results in the transfer of the capacity for propagation to another monomer.

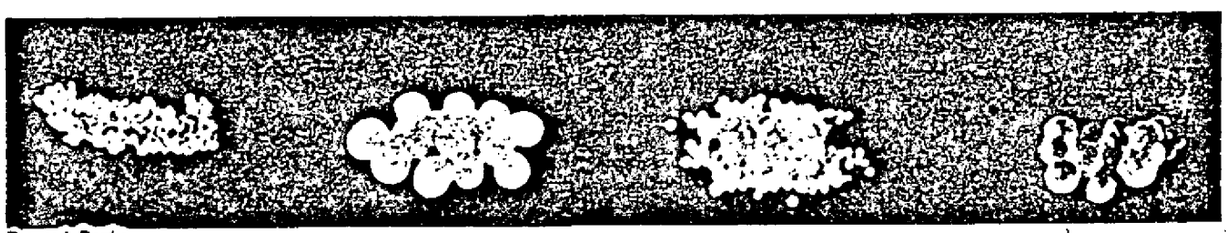
The third elementary reaction is the *termination* of the growing chains either by mutual saturation of the activated ends or by collision with molecules of the solvent or of any kind of deactivating impurities (1, 3, 11-14).

Finally, there are other processes, such as chain transfer (8, 12, 37, 39, 40) branching, or cross-linking which eventually interfere and result in the production of more complicated macro-molecules.

It has been possible to derive equations which, in homogeneous systems, allow the description of the interaction of activation, propagation, and termination and make it possible to precalculate the initial rate of monomer consumption and the number average polymerization degree of the reaction product in fair agreement with the experimental facts (1, 9-11, 14, 16, 21, 41). This may encourage the attempt to extend this kind of kinetic treatment to polymerization in heterogeneous systems.

The most common types of heterogeneous polyreactions are polymerizations in suspension and emulsion (11, 41-43). Particularly the latter is of great practical value. There exists an extensive patent literature on it (examples of which are 34, 44, 45); while only few articles have appeared up to date in scientific magazines or books (41, 42, 43), the most informative of which is a recent

[1] Polytechnic Institute of Brooklyn, Brooklyn, N. Y.
[2] Bibliography references appear at the end of the article.



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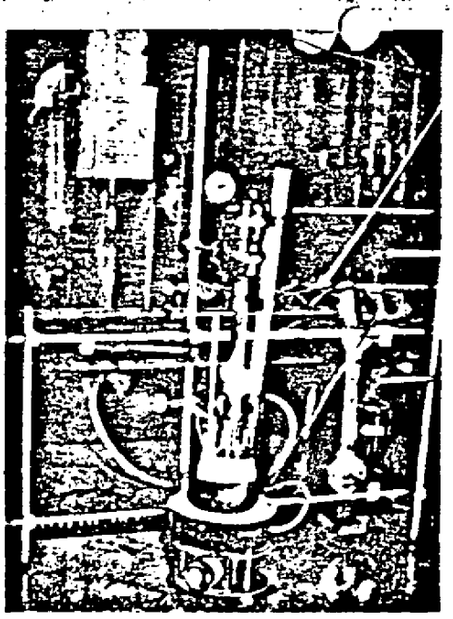

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Fig. 2. Reactor Flask Used with High Boiling Monomers

paper by C. F. Fryling and E. W. Harrington (42). However it seems that the conditions for emulsion polymerization are more complex than those of the polymerization of a vinyl derivative in aqueous suspension, where, without the use of any emulsifying agent, macroscopic globules of easily measurable size (diameter between 0.1 and 10 millimeters) can be produced and maintained. It was therefore felt that a number of preliminary measurements on suspension polymerization might not be out of place. This article intends to give a qualitative description of the general procedure in "pearl" or "bead" polymerization; while another paper will try to propose a somewhat quantitative treatment of such processes.

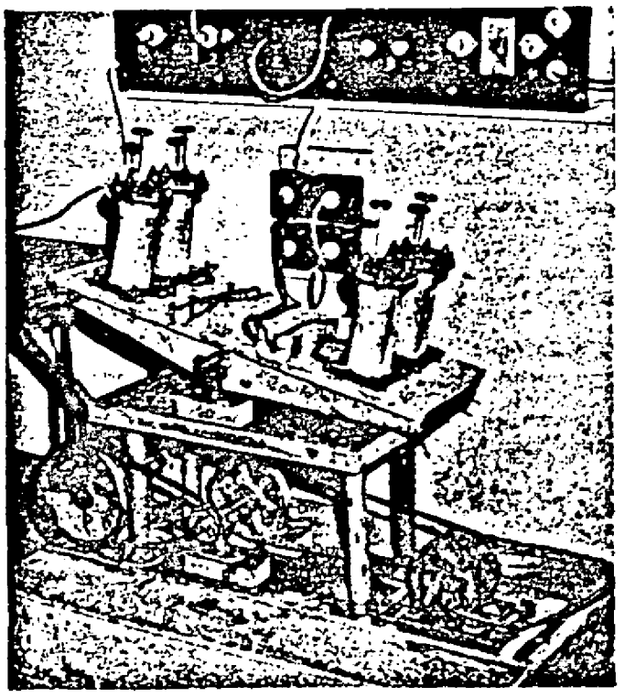

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Fig. 3. Autoclaves and Agitating Mechanism for Low Boiling or Gaseous Monomers

In addition to these basic investigations that have been carried out in this laboratory during the last three years, the properties of the polymers produced by this method were studied. From a commercial point of view it appears that certain advantages might be expected from "pearl" polymerization. The procedure as such is simple, and the polymer is obtained in an easily manageable form. Temperature control is comparatively easy, and the homogeneity and purity of the product represent appealing features.

Figure 1 shows as an example a number of globular products as obtained by this procedure, and Table 1 gives a few representative figures of these materials.

TABLE 1. PROPERTIES OF "PEARL" POLYMERS

Material	Average Globular Size in Mm.	Average Molecular Weight	Appearance	Characteristics
Styrene	1½	85,000	Transparent	Hard, brittle
Styrene	¾	78,000	White, opaque	Hard, brittle
Chlorostyrene	2	67,000	Yellow, translucent	Hard
Chlorostyrene	½	78,000	Yellow, transparent	Hard

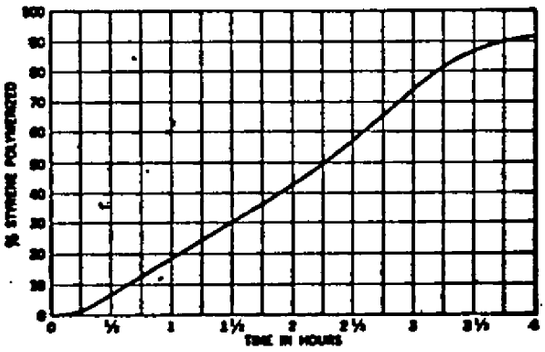

Fig. 4. Example of Suspension Polymerization Rate with Styrene

Experimental Conditions

The principle of this type of polymerization is that the liquid monomer is being dispersed in a non-solvent (in most cases water or aqueous solutions) by strong mechanical agitation and that polymerization takes place inside the small suspended globules. This eliminates the use of surface active materials and produces fairly pure substances since the globules themselves do not contain anything but the polymer and traces of a catalyst. It was soon found that, in general, mechanical agitation is not sufficient to prevent the monomer globules from coalescing at some time during the course of the reaction. It became evident that it would be advantageous to add certain substances to act as *suspension stabilizers*. Several patents (including 45) describe and protect the use of such stabilizers which may be of organic or inorganic origin. They do not stick permanently and closely to the final polymers, as soap or other surface active materials do, and can be easily removed at the end of the reaction by adequate washing or filtering processes.

A rather simple experimental arrangement can be employed. The polymerization is carried out in a three-neck flask, equipped with mercury seal stirrer, condenser, and thermometer. Figure 2 shows one of these flasks which has performed fairly satisfactorily. They could, of course, be used only for monomers whose boiling points lie above the reaction temperature. For the polymerization of lower boiling or gaseous monomers electrically heated autoclaves run on a shaking machine are necessary (compare Figure 3).

In the following we shall give some information about producing and polymerizing suspensions of various types. Different materials can be used to prevent the globules from agglomerating into a lump, and each one has its optimum proportions. One characteristic of a given suspension stabilizer is its capacity to maintain a certain definite average size of the polymerizing spheres in the suspension. Inefficient suspension stabilizers favor the formation of lumps when used in small proportions; while very large globules appear if higher proportions are employed. Table 2 illustrates some formulations and their merits.

TABLE 2. EFFECT OF DIFFERENT STABILIZERS ON SIZE OF "PEARL" POLYMERS

Grams Water	Grams Hydrocarbon	Catalyst %	Stabilizer	—%	Temperature—°C.	Hours	Globular Size/in Mm.
300	50	1	Talc	0.8	90-95	6	1
300	50	1	Polyvinyl alcohol	0.5	90-95	4	3
300	50	1	Gelatin	0.8	90-95	6	2
300	50	1	Bentonite	3.0	90-95	6	3

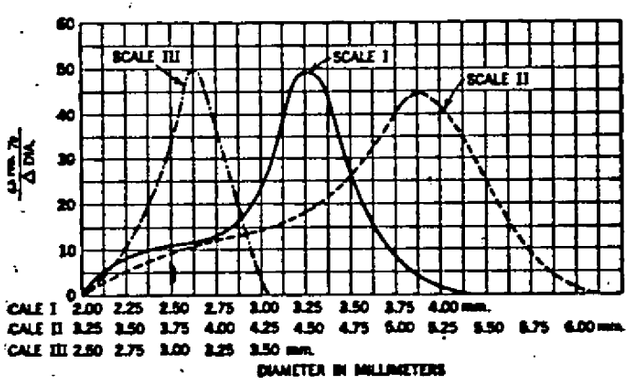

Fig. 5. Polymer Size Distribution Curves for Suspension Polymerized Styrene

Catalysts, or rather initiators or activators, indicated for this method of polymerization are mainly of two types: namely, hydrocarbon soluble organic peroxides and water soluble inorganic peroxides or salts of peracids. It was observed that contrary to the experiences with emulsion polymerization the hydrocarbon soluble types proved distinctively more effective. (See Table 3.) A series of experiments carried out with styrene and benzoyl-peroxide at 90° C. showed that the rate of the reaction increased with the amount of peroxide used and that under the conditions prevailing in these runs the main part of the reaction takes place between the second and third hour.

TABLE 3. EFFECT OF SOME ORGANIC AND INORGANIC PEROXIDE ACTIVATORS ON STYRENE "PEARL" POLYMERS

Grams Water	Grams Styrene	Talc %	Benzoyl Peroxide	Potassium Persulphate	Sodium Perborate	Temperature °C.	Hrs.	Result
300	50	0.8		2%*		90	3	Stable suspension; little polymer formed
300	50	0.8	2%*			90	3	Polymer globules formed
300	50	0.8			2%*	90	3	Polymer formed
300	50	0.8			2%†	90	13	Little polymer formed

* % on weight of monomer.
† The initiator was added in three portions in one-hour intervals.

The ratio of water to hydrocarbon is of relatively small importance as long as one works with a sufficient excess of the aqueous phase. Favorable conditions [illegible]

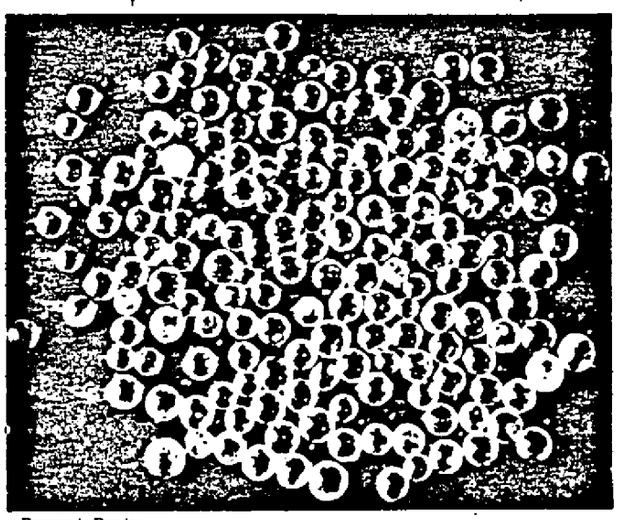

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Fig. 6. Styrene "Pearls" of Varying Degrees of Transparency

if one has between three and six times as much water as hydrocarbon. Higher proportions of monomer interfere with proper dispersion and make the temperature control more difficult.

Benzoyl peroxide initiates styrene polymerization in dispersion at temperatures above 50° C. (2, 14, 35, 36). The polymerization temperature is limited by the softening point of the polymer. Approaching it, the globules tend to merge and to yield lumpy masses which do not polymerize homogeneously and include some of the suspension stabilizer. In our experiments, therefore, temperatures of about 10° below the softening range of the reactant materials were used.

The pH of the aqueous phase has a definite influence on the ease of "pearl" formation. Alkaline conditions up

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Fig. 7. Styrene "Pearl" Polymer before (left) and after Swelling

to a pH of 10 do not interfere with the formation of pearls; while reduction of the pH even to 5.0 proves detrimental to the reaction.

Keeping the above points in mind it is comparatively easy to control the course of a "pearl" polymerization and to obtain globular polymers of any desired size.

The Suspension Polymerization Reaction

"Pearl" polymerization takes place in three rather definite steps. There is a first period during which the dispersed globules of the monomer remain liquid and show little or no tendency to coalesce as long as stirring is continued. This part of the reaction roughly corresponds to the induction period as observed in other polymerization processes. During the second step some polymer is formed in the globule and dissolves in the monomer, thus producing gummy and sticky particles which tend to merge with each other. Finally polymerization throughout the globule is more or less completed. The second (sticky) period is most critical for the outcome of the reaction since during it colloiding spheres are liable to agglomerate. At the beginning, while the reaction mass is still fairly fluid, such coalesced spheres are quickly broken up again, and toward the end the globules do not stick together as long as the temperature is kept below the softening point of the product.

Whether a particular material polymerizes in well-defined "pearls" or whether it lumps together seems to depend upon the stirring, the nature of the suspension stabilizer, and the difference between the density of the aqueous medium and the monomer. Best results are obtained by adjusting these three contributing factors carefully to an optimum degree. It seems that the finely dispersed stabilizers adhere to the surface of the spheres, and form a layer around them preventing coagulation, upon collision during the sticky period of the reaction. Superimposed on this phenomenon is the fact that an increased density of the aqueous medium helps prevent localization of the globules in one particular zone of the liquid. It is possible to carry out polymerization of monomers, such as styrene, acrylic derivatives, isoprene, etc., in aqueous salt solutions of various densities and in mixtures of water and glycols or glycerol.

The mechanism of the reaction seems to be essentially one of bulk polymerization (12, 21, 37). Only hydrocarbon soluble initiators, as benzoyl or lauryl peroxide, start the reaction effectively at temperatures between 40° and 80° C; while water soluble catalysts, such as hydrogen peroxide or sodium persulphate, are less effective. Also water soluble activators do not accelerate the peroxide catalyzed reaction noticeably. Qualitatively, it is apparent that the overall rate of monomer consumption, which is equivalent to polymer formation, is approximately proportional to the square root of the concentrations of the hydrocarbon soluble catalyst. This points to a radical chain mechanism for the reaction inside each individual globule. Owing to the small mass of monomer in the globules and to their extensive cooling by the aqueous medium, the temperature in the globules does not undergo significant variations. All this tends to show that "pearl" polymerization may be considered as a bulk polymerization with effective water cooling. It must be pointed out, however, that the rate of monomer consumption in suspension seems definitely greater than in bulk under equivalent conditions. We shall discuss in greater detail in another communication possible causes for this phenomenon. Here we wish to indicate only that it seems to be connected with an increased rate of nuclei formation in the case of "pearl" polymerizations. As an example of the speed of a reaction, Figure 4 describes a run of styrene at 85° C. and the amount of polymer formed at various time intervals.

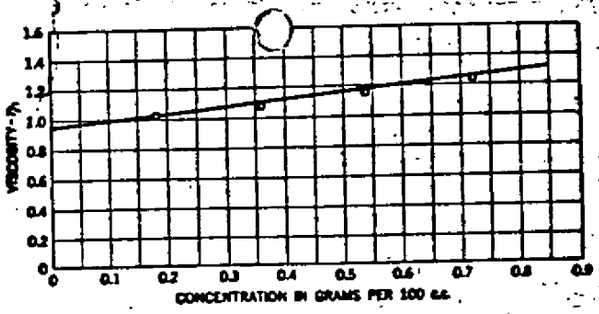

Fig. 8. Intrinsic Viscosity vs. Concentration for Styrene "Pearl" Polymers

The Resulting High Polymer

The polymers obtained in small-scale runs consist in most cases of rather perfect globules of fairly uniform size. Figure 5 gives the size distribution curves of three different batches of polystyrene. It is significant that in each of these curves the largest percentages of spheres occur in a relatively narrow size range, and the largest globules have diameters approximately twice that of the smallest. Depending upon the nature of the stabilizer and the final percentage conversion of monomer, the globules may be completely water clear (Figure 6), approaching in appearance the best block polymers, or may exhibit white opacity or all the intermediate degrees of translucency.

Mechanically the "pearls" can be hard, soft, or rubbery, depending upon the monomer or combination of monomers. Styrene and acrylic esters yield hard globules which exhibit considerable elasticity and toughness. These polymers are soluble in the usual solvents; while diene polymers or materials containing a diene yield insoluble spheres that show a distinct swelling in many liquids. Figure 7 shows such a "pearl" polymer swollen and suspended in toluene. This material is rubbery and semi-transparent and apparently consists of globules which are cross-linked to a considerable extent. If carried out in bulk, such a copolymerization leads to an insoluble and infusible gel which is very difficult to remove from the reaction vessel. "Pearls" of this material, however, can be easily removed from the reaction flask and represent a material which offers no difficulties for rolling or calendering operations.

In order to get an idea of the degree of polymerization of some styrene "pearl" polymers, the viscosity average molecular weight was determined (39-41, 46, 47). Solutions of the polymer in toluene ranging from 0.2-0.8% were made, and their viscosities measured in the usual way. The intrinsic viscosities of the solutions were obtained by extrapolating the η sp/c *versus* concentration graph (see Figure 8) and the molecular weights computed from the equation: $[\eta] = KM^a$, using for K and a the values of 10^{-2} and 0.72 respectively. Table 4 gives a few examples of molecular weights of polystyrene "pearls" and shows that the molecular weight is of the order of magnitude of 85,000 even under somewhat varying reaction conditions.

TABLE 4. MOLECULAR WEIGHTS OF STYRENE "PEARL" POLYMERS

Grams Styrene	Grams Water	% Suspension Stabilizer	% Catalyst	Time Hours	Temperature °C.	Molecular Weight
50	500	Talc 1	1.0	3	85	85,000
50	500	Bent. 3	0.5	15	75	80,000
50	500	Bent. 3	1.0	15	75	83,000
50	500	Bent. 3	0.75	19	75	85,000
50	500	Bent. 3	1.0	48	65	93,000

Conclusions

To achieve polymerization in suspension specific reaction conditions have to be worked out for each monomer.

The polymerization itself seems to proceed like an effectively cooled, speeded-up bulk polymerization.

The resulting high polymers appear in the form of regularly formed spheres of controlled and fairly uniform size. They may be translucent or opaque, hard, soft, or rubbery, soluble or only swellable according to the monomor or combinations of them. The average molecular weights of polystyrene "pearls" under prevailing reaction conditions are around 100,000.

The authors wish to thank the Whitney Blake Co., Hamden, Conn., for making this research work possible and especially wish to extend their thanks to J. H. Ingmanson, R. Dudley, and J. Wulff for their most valuable cooperation.

Bibliography

(1) J. Abere, G. Goldfinger, H. Naidus, and H. Mark, *Ann. N. Y. Acad. Sci.*, 44, 267-96 (1943).
(2) H. N. Alyea, J. J. Gartland, and H. R. Graham, *Ind. Eng. Chem.*, 34, 458, (1942).
(3) J. L. Bolland, *Proc. Roy. Soc.* A178, 24 (1941).
(4) J. W. Breitenbach and R. Raff, *Monatsh.*, 69, 1107 (1936).
(5) J. W. Breitenbach and H. Rudorfer, *Monatsh.*, 70, 37 (1937).
(6) R. E. Burk, L. Laskowski, and H. R. Lankelma, *J. Am. Chem. Soc.*, 63, 3248, (1941).
(7) W. H. Carothers, "Collected Papers", Interscience Publishers, New York, 1940.
(8) P. J. Flory, *J. Am. Chem. Soc.*, 59, 241 (1937).
(9) R. Ginell and R. Simha, *Ibid.*, 65, 705, 715 (1943).
(10) H. Hulburt, R. A. Harman, A. Tobolsky, and H. Eyring, *Ann. N. Y. Acad. Sci.*, 44, 371 (1943).
(11) H. Mark and S. Raff, "High Polymeric Reactions", Interscience Publishers, 1941.
(12) H. W. Melville, *Trans. Far. Soc.*, 32, 258 (1936); *Proc. Roy. Soc.* A165, 263, 511, (1937); A167, 99 (1938).
(13) R. G. W. Norrish and R. R. Smith, *Nature*, 150, 336 (1942).
(14) C. C. Price, *Ann. N. Y. Acad. Sci.*, 44, 351 (1943).
(15) W. Kern and H. Kammerer, *J. prakt. Chem.*, (2) 161, 300 (1942).
(16) G. V. Schulz, A. Dinglinger, and E. Husemann, *Z. physik. Chem.*, B43, 25, 47, 385 (1939); B50, 305 (1941).
(17) H. Staudinger and G. V. Schulz, *Ber.*, 68, 2320 (1935).
(18) G. S. Whitby, *Trans. Far. Soc.*, 32, 315 (1936).
(19) G. S. Whitby and R. M. Croxier, *Can. J. Research*, 6, 203 (1932).
(20) G. S. Whitby and M. Katz, *J. Amer. Chem Soc.*, 50, 1160 (1928).
(21) J. W. Breitenbach, *Monatsh.*, 71, 275 (1938).
(22) J. W. Breitenbach, *Z. physik. Chem.*, B45, 101 (1939).
(23) J. W. Breitenbach and H. Maschin, *Ibid.*, A187, 175 (1940).
(24) G. Gee, *Trans. Far. Soc.*, 34, 712 (1938); 36, 1171 (1940).
(25) G. Gee, C. B. Davies, and H. W. Melville, *Ibid.*, 35, 1298 (1939).
(26) H. W. Melville, *Trans. Inst. Rubber Ind.*, 15, 209 (1939).
(27) H. W. Melville and J. L. Bolland, *Cent. Chem. Ztg.*, 42, 201 (1939).
(28) H. W. Melville and T. T. Jones, *Proc. Roy. Soc.*, A175, 392 (1940).
(29) H. W. Melville, T. T. Jones, and R. F. Tuckett, *Chem. Ind.*, 59, 267, (1940).
(30) H. Pfann, Master's thesis, Polytechnic Institute of Brooklyn, 1942.
(31) C. C. Price and R. W. Kell, *J. Amer. Chem. Soc.*, 63, 2798 (1941).
(32) C. C. Price, R. W. Kell, and E. Krebs, *Ibid.*, 64, 1103 (1942).
(33) S. Abkin and S. Medvedev, *Trans. Far. Soc.*, 32, 286 (1939).
(34) British patent No. 427,494 (1934).
(35) R. E. Burk, B. G. Baldwin, and C. H. Whitacre, *Ind. Eng. Chem.*, 29, 326 (1937).
(36) A. C. Cuthbertson, *Can. J. Research*, 20, 103 (1942).
(37) G. V. Schulz and E. Husemann, *Z. physik. Chem.*, B34, 187 (1936); B36, 184 (1937); B34, 246 (1938).
(38) O. Mamontova, S. Abkin, and S. Medvedev, *Acta Physicochim, U. R. S. S.*, 12, 269 (1940).
(39) T. Alfrey, Ph.D. thesis, Polytechnic Institute of Brooklyn, 1943.
(40) R. F. Boyer and R. D. Heidenreich, "Electron Microscope Studies with High Polymer Solutions", lecture given at the Electron Microscope Symposium, New York, Jan., 1944.
(41) H. Fikentscher, *Angew. Chem.*, 51, 433 (1936).
(42) C. F. Fryling and E. W. Harrington, *Ind. Eng. Chem.*, 36, 114 (1944).
(43) E. Trommsdorf, *"Chemie und Technologie der Kunststoffe"* by R. Houwink, p. 320, Akademische Verlagsgesellschaft M.B.H., Leipzig (1939).
(44) British patent No. 455,742 (1936).
(45) United States patents Nos. 2,108,044 (1938) and 2,194,334 (1940).
(46) A. Bartovics and H. Mark, *J. Amer. Chem. Soc.*, 65, 1901 (1943).
(47) P. J. Flory, *Ann. N. Y. Acad. Sci.*, 44, 419 (1943).
(48) M. L. Huggins, *J. Phys. Chem.*, 46, 151 (1942).

The Formation of Vinyl Polymers in Emulsions and in Suspensions—III

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The Formation of Vinyl Polymers in Emulsions and in Suspensions—III

Experiments on the Polymerization of Styrene in Agitated Emulsions . . .

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IN TWO previous short papers (1, 2)[3] a few experiments on the polymerization of styrene in unagitated aqueous solution, suspension, and emulsion were reported. This article intends to present some data concerning the same reaction in *agitated* emulsions.

To get a preliminary insight into the mechanism of such emulsion polymerizations it becomes first of all necessary to carry them out under controlled conditions in a reproducible way. This is by no means simple. While it is comparatively easy to reproduce individual polymerization runs of styrene in solution or in the pure monomer phase regarding the amount of polymer formed at a given instant to within a few per cent., it is a rather difficult task to get a reproducibility better than 10 or 12% in emulsion. We therefore believe that the following experiments have only the character of an exploratory and orienting study, which allows the drawing of certain general conclusions on the reaction mechanism and which makes it clear how better experiments should be planned for a more conclusive investigation.

As a polymerization reaction in emulsion proceeds, the following quantities are becoming subject of measurement:

1. The amount of polymer formation during a certain time period.
2. The average degree of polymerization of this polymer.
3. The molecular weight distribution curve of this polymer.
4. The average particle size of the emulsion at any given time.
5. The particle size distribution curve of the emulsion at any given time.
6. The amount of catalyst left and the pH at any given time.

In the following we shall present a few experiments dealing with points 1, 2, and 4 and add some remarks about points 3 and 5. The change of pH during the emulsion polymerization of acrylonitrile has been recently followed and discussed by Fryling and Harrington (3).

Amount of Polymer Formation

A number of styrene emulsions with different average initial particle size were prepared by varying the amount of ammonium oleate in the system. Table 1 gives a survey of the emulsions used for these measurements. Aliquot parts (36 milliliters) of these emulsions were introduced into test tubes (of about 50-milliliter capacity) which had been drawn out into a thin neck of about three millimeters diameter. The catalyst was then added; the tube sealed and put in a shaking device, which operated at constant temperature with the moderate speed of 50 shakings a minute. It should be mentioned here that the speed and mode of shaking are of considerable influence on the shape of the conversion curve and also on the total amount of monomer converted. We carried out all observations in the same shaking machine with the same rate of about 50 shakings a minute, but did not carry out any systematic investigation of the influence of rate or mode of shaking on the rate and amount of conversion. The tubes were withdrawn at definite time intervals; the necks opened and the contents poured into a dilute solution of acetic acid to break the emulsion. The coagulated polymer was filtered off and washed several times with methanol. Then it was redissolved in methylethyl ketone, reprecipitated with methanol and repeatedly washed with methanol and water until the washings were free from monomer, catalyst, or soap. The product was then dried and weighed.

The reproducibility of this method was tested by withdrawing several ampules at the same time and comparing the amounts of polymer formed. At low conversions (up to 20 or 25%) considerable variations were encountered, but as the reaction proceeded, the results could be reproduced to about 10 or 15%. Vinograd (4) recently studied the polymerization of soap-solubilized styrene with the pycnometer method, which offers the advantage of continuous observation and, very presumably, also of better reproducibility.

TABLE 1. CHARACTERISTICS OF THE STYRENE EMULSIONS USED

All emulsions contained: 180 ml = 10 mols water
19 gram = 0.18-mol monostyrene
2.8 gram = 0.034-mol sodium perborate
Molar ratio water to monomer 55.5
Molar ratio monomer to catalyst 5.3

The emulsions contained the following amounts of ammonium oleate:

Run No.	Grams of Soap	Mols of Soap	Molar Ratio—Monomer/Soap	Molar Ratio—Soap/Monomer
1	0.9	3.0×10^{-3}	60	1.67×10^{-2}
2	1.0	3.3×10^{-3}	54.5	1.83×10^{-2}
3	1.1	3.6×10^{-3}	50	2.00×10^{-2}
4	1.2	4.0×10^{-3}	45	2.22×10^{-2}
5	1.3	4.3×10^{-3}	42	2.38×10^{-2}
6	1.4	4.6×10^{-3}	39	2.56×10^{-2}
7	1.5	5.0×10^{-3}	36	2.78×10^{-2}

Figure 1 shows some conversion curves of emulsions with different initial average particle radii (0.4, 1.6, and 3.6 microns). It can be seen that all curves have a definite inhibition period which increases with the initial particle size of the emulsion. An inhibition period was to be expected because, firstly, the monomer presumably still contained traces of stabilizers or other impurities and, secondly, air was present in these experiments. It seems that in emulsions which contain more soap and hence on the average smaller particles, the inhibitors are more rapidly disposed of than in less highly dispersed systems. Several reasons can be offered for this effect.

If the inhibitor is monomer soluble, it will take more time to diffuse out of a large globule than out of a small one; hence the critical inhibitor concentration at which the reaction proceeds rapidly is reached sooner in a highly dispersed emulsion. If the inhibitor is water-soluble, it may be that it is more rapidly destroyed in systems having a large specific interface area or it may be that emulsions containing a higher soap-monomer ratio are capable of a faster nucleus formation and, therefore, consume the inhibitor more rapidly. The last explanation would be supported by Fryling's (3) views of the action of the soap micelles and by Vinograd's (4) measurements of the heat of activation of nuclear formation in soap solubilized styrene.

The inhibition period can be reduced by using highly purified monomer and by excluding oxygen from the system as much as possible (comp. 2), but we have no systematic results to offer in this respect as yet.

If one takes samples from the same emulsion (containing the same amount of inhibitors) and runs them at different temperatures, a significant decrease of the length of the inhibition period with increasing temperature is observed. Using the same an-

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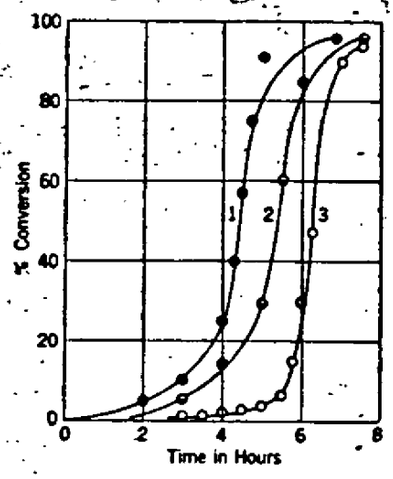
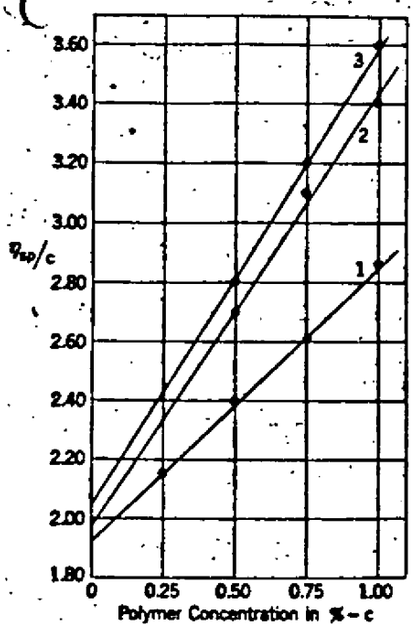


Fig. 1. Conversion Curves for Emulsion of Different Initial Particle Size



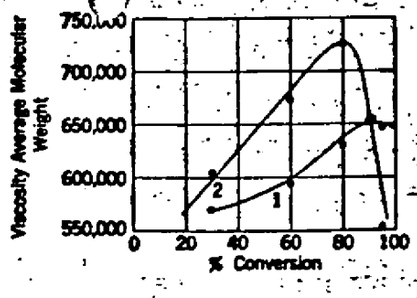


Fig. 3. Average and Instantaneous Molecular Weight of Five Samples

(Left)

Fig. 2. Intrinsic Viscosities of Three Fractions of a Polymerization

(2) one obtains for the activation energy of the initiation reaction values between 15,000 and 18,000 cal per mol. This seems to indicate that the initiation process in these agitated systems has about the same energy requirement as has been deduced by Vinograd (4) from the initial rate of the polymerization of styrene in unagitated soap solutions and by Frilette (5) from the inhibition period in such solutions.

Average Degree of Polymerization of the Polymer Formed

After the samples had been weighed, they were used to measure the viscosity average molecular weight of the polymer formed up to the instant of the withdrawal of the sample. In view of the orienting character of the whole investigation, no osmotic pressure or light scattering measurements were carried out, but the *intrinsic viscosity* was used to determine the viscosity average molecular weight. For this purpose the viscosities of four or five solutions of each sample were measured at 40° C. in toluene within the concentration range between $c = 0.2$ and $c = 1.0\%$, and the specific viscosities η_{sp} computed. Graphs of $\frac{\eta_{sp}}{c}$ *versus* c were then made, and by a straight line extrapolation the intrinsic viscosity $[\eta]$ of each sample was determined. Figure 2 shows as example one graph, representing three polymers withdrawn from a run at 4.75, 5.00, and 5.50 hours, which was started with 180 milliliters of water, 19 grams of monostyrene, and 1.4 grams of soap and polymerized at 70° C. This run is No. 6 in Table 1. The intrinsic viscosities of the samples are 1.92, 1.97, and 2.04 respectively.

These values were then converted into viscosity average molecular weights M by the equation

$$[\eta] = 1.22 \times 10^{-4} \times M^{0.75} \qquad (A)$$

The two constants in equation (A) were chosen from values available in the literature. We are very much indebted to L. Drake and R. Spencer, of the research department of Dow Chemical Co., Midland, Mich., who recently carried out more precise recalculations of these constants and recommended to us the above values. It must, however, be pointed out that all the polymers for which comparative osmotic (or light scattering) and viscosity measurements have been carried out and for which, therefore, values for the constants in equation (A) are available have been prepared either in the pure monomer phase or in a homogeneous solution. It is not impossible that a polymer formed in emulsion requires another set of constants, and we, therefore, do not think that the *absolute values* of the viscosity average molecular weights, as reported here, are very reliable. We believe, however, that the *relative* magnitude of these values is sufficient to allow the few conclusions which will be drawn from them in this section.

Table 2. Viscosity Average Molecular Weights M for the Polymers Withdrawn at Different Times during Several Runs

Run No.	M Estimated from Intrinsic Viscosity after 4½ Hrs.	5 Hrs.	5½ Hrs.	6 Hrs.	7 Hrs.
1	.....	.....	.....	1,140,000	1,160,000
2	.....	.....	870,000	1,130,000	1,110,000
3	500,000	570,000	580,000	720,000	1,100,000
4	.....	570,000	590,000	630,000	645,000
5	930,000	960,000	1,100,000	.....	.....
6	580,000	640,000	800,000	.....	.....
7	1,100,000	900,000	.....	.....	.....

Table 2 contains the viscosity average molecular weights M of samples withdrawn at different times from runs No. 1 to No. 7, as listed in Table 1. It can be seen that in most cases (except runs 2 and 7) the viscosity average molecular weight (as measured here) increases as the conversion of monomer into polymer increases. The maximum viscosity average molecular weights of five runs (Nos. 1, 2, 3, 5, and 7) are of about the same order of magnitude: namely, 1,100,000;[4] while runs 4 and 6 yielded materials of a lower degree of polymerization. We cannot give any reasonable explanation for this fact because there was no evidence for any irregularity during these two runs as compared with the other five. This is one of the frequent instances in which uncontrollable effects occur during emulsion polymerization and which certainly call for further investigation and clarification.

The figures of Table 2 represent the M-values of the polymer formed *up to a certain time t or conversion z*. In order to correlate them with the conversion curve as discussed in the previous paragraph, they have to be transformed into differential or *instantaneous* values: namely, into the molecular weights of the polymer formed during a given period, say between the fifth and sixth hour of the reaction or between 55 and 65% conversion. The time average $\overline{M}$ of the viscosity average molecular weight M up to a conversion z is obviously given by

$$\overline{M} = \frac{1}{z}\int M(z)\,dz \qquad B$$

where M(z) is the instantaneous viscosity average molecular weight formed at the conversion z. Differentiating (B) with respect to z one obtains

$$M(z) = \overline{M} + z\,\frac{d\overline{M}}{dz} \qquad C$$

[4] If one would use the Staudinger equation $[\eta] = K_m M$ and apply a K_m value of 4.5×10^{-4}, the maximum molecular weight obtained during these runs would be about M = 455,000.

order to compute $M(z)$ as a function of z, one first plots values of $\overline{M}$, as indicated in Table 3, *versus* z and obtains 1 of Figure 3. Then after graphical estimation of $\frac{d\overline{M}}{dz}$ ses equation (C) to calculate $M(z)$ as a function of z. is indicated in Figure 3 by curve 2. Comparing curve 2 gure 1 with curve 2 of Figure 3, it can be seen that the ular weight of the polymer formed during the period im- tely after the start of the conversion (before the fifth —*acceleration* period—is comparatively low. This can plained by the presence either of traces of inhibitor or of inbreaking addition compound between inhibitor and acti- monomer. As the reaction reaches its full rate between 5½ and $t = 6½$, the molecular weight of the polymer ed at that time increases, and it is only during this period the chains grow out to their proper length, and a material aximum DP is produced. It must be emphasized that each taneous molecular weight is still a viscosity average over species, because even under exactly defined macroscopic tions, such as concentration of monomer, catalyst, inhibitor, different active centers will grow out to chains of different h because of the statistical nature of all molecular processes. polymer *at each given conversion* z is therefore already a ure of chains of different length. To this heterogeneity is superimposed the non-uniformity of the polymer formed e *different periods* of the reaction as shown by curve 2 in re 3.

TABLE 3. TIME AVERAGE AND INSTANTANEOUS MOLECULAR WEIGHT OF SEVERAL SAMPLES

No. 4; Five Samples Withdrawn between $t = 5$ Hours and $t = 7$ Hours

Time of Withdrawal Hours	% Conversion z at That Time	$\overline{M}$ from $[\eta]$	$\frac{d\overline{M}}{dz}$	$\overline{M}(z)$ of Polymer Formed at That Time
.....	30	570,000	+ 1300	610,000
.....	60	590,000	+ 1300	670,000
.....	80	630,000	+ 1300	725,000
.....	90	655,000	around zero	655,000
.....	95	645,000	— 4000	550,000

l this contributes to the fact that the final polymer, as mulated throughout the whole reaction, is a rather in- ogeneous material and, particularly, contains a considerable unt of chains of inferior length, which according to recent ies of Harris (6), Kemp (7), and their collaborators may be detrimental for certain mechanical properties of the erial. In most of our runs the viscosity average molecular ht of the polymer formed up to a certain time increased ly, but steadily during the reaction, indicating that a material ncreasing DP is produced as the conversion proceeds. In e cases, however, it was found that, as the reaction pro- s further (conversions around and above 90%), $M(z)$ eases again and eventually assumes rather low values toward end of the run. There are presumably several factors which ribute to this effect; two of them are the following:

a) As more monomer is consumed, its concentration de- ses and reaches comparatively low values around and above conversion. In homogeneous systems the rate of the agation reaction depends upon monomer concentration of exponential power between 1.5 and 2.0; while the different ination reactions depend upon monomer concentration of exponential power between 0.5 and 1.0. Responsible for the age molecular weight is the ratio of rate of propagation rate of termination, which is roughly proportional to the power of the monomer concentration. Hence decreasing omer concentration depresses the average molecular weight the polymer formed. This conclusion, of course, cannot rigorously applied to emulsion polymerization, the kinetics which is not known, but it seems not unreasonable to me that, in general, a decrease in monomer concentration always lead to a lower molecular weight.

b) During the whole course of the reaction, decomposition ducts of the catalyst (mainly oxygen) can act as chain- kers or transfer catalysts and therefore influence the degree olymerization of the product. It is conceivable that toward end of the reaction there are relatively more such decom- ition products present per unit number of growing chains at lower conversions. This leads to a lower number (and also viscosity) average molecular weight of the polymer formed during this last period of the polymerization.

The ideal situation would be if $\overline{M}$ were represented by a horizontal straight line in the graph of Figure 3, because then the second term in equation (C) vanishes, and the instantaneous molecular weight $M(z)$ becomes constant and equal to the $\overline{M}$; the same type of polymer would be produced throughout the reaction. This, however, seems practically never to be the case in emulsion polymerizations, which have conversion curves of the type shown in Figure 1.

Another indication of the distinctly heterogeneous nature of the polymer formed in the course of such a reaction can be obtained in the following way. The samples withdrawn from run No. 1 after six and seven hours have intrinsic viscosities of 2.57 and 2.87 respectively and consequently (as shown in Table 2) have molecular weights which are not far apart from each other. However if one follows the procedure of Huggins (8) and computes from the slope of their respective $\frac{\eta_{sp}}{c}$ *versus* c plots the k' constants characteristic for these two polymers, one arrives at values of 0.37 and 0.28 respectively. In the sense of Huggins' interpretation and of previous investigations by Flory (9) on polyisobutylene, Alfrey and Bartovics (10) on cellulose acetate and polystyrene, the k' constant characterizes a polymer solution with respect to the mutual hydrodynamical interaction between the molecules of the solvent and the sub-molecules of the polymer. If the two samples of run No. 1 have similar average degrees of polymerization, but widely different k' values, as they do have, it may be interpreted that either the molecular-size distribution is different or that the two polymers differ from each other in certain structural details of the chain. Another similar case is encountered if one compares the k' constants of the 4½-hour and 5-hour samples of run No. 5 (compare Table 2) which have very much the same average molecular weight, but distinctly different k' values: namely, 0.26 and 0.39 respectively.

These samples, as well as those of run No. 1, also show qualitatively rather different solubility characteristics. If one prepares a 1% solution of each in methylethyl ketone and adds methanol, the first precipitate appears at distinctly different amounts of methanol added, and the behavior of the two solutions throughout the precipitation is different.

The next logical step would have been to work out complete molecular weight distribution curves of the samples withdrawn at certain times during the different runs. These samples, however, were in most cases too small for such a further-going analysis, and we did, therefore, postpone this more elaborate study of the composition of the polymer formed up to a certain conversion. A knowledge (even approximate) of the molecular weight distribution curve of the polymer formed during the different periods of the reaction would be of considerable value for the interpretation of what happens during each of these periods.

Average Particle Size of the Emulsions

Another interesting question was how the average particle size of an emulsion and its size distribution curve affect the course of the polymerization reaction and whether the average size of the emulsified monomer particles remains constant throughout the process or changes as the liquid monomer is converted gradually into solid polymer. It was known from previous industrial work with emulsions of the Buna S and Buna N type that their average particle size is considerably smaller than that of rubber in native latex, and it is qualitatively apparent that the average particle diameter decreases during polymerization. The initial emulsions, as prepared by shaking the pure liquid monomer with a dilute soap solution, usually have a creamy color, which after polymerization shows a distinct bluish tint, indicating that during the reaction the degree of dispersion of the colloidal system has been increased.

There are several ways of investigating the average particle diameter of such suspensions and even to arrive at an approximate form of the particle size distribution curve of which the use of the optical dark-field microscope (11-12) and of the

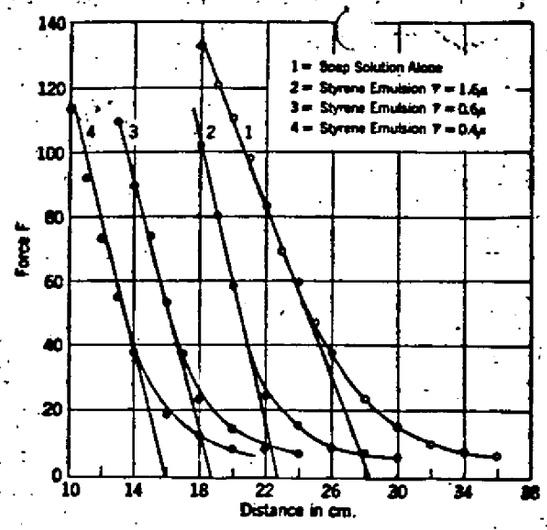


Fig. 4. Compression Curve of a Soap Solution and of Three Emulsions

electron microscope (13) have been repeatedly demonstrated with great success. Considering the orienting character of this investigation, however, we felt that it would be recommendable to select a less time-consuming and complicated procedure in order to be able to determine approximately the fineness of a large number of emulsions at various degrees of conversion during the progress of polymerization. We therefore used a spreading method outlined a few years ago by Davey (14), which seems to give results quickly and reproducibly. They agree, at least in the first approximation, reasonably well with those of a direct optical or electronoptical counting.

The procedure follows: One uses a normal hydrophilic Langmuir balance and first determines the area which a certain volume (e.g., 0.01-milliliter) of a pure dilute soap solution requires because of the spreading of the surface active ammonium oleate. Curve 1 in Figure 4 shows a compression curve carried out with 0.0112-milliliter of a 0.5% ammonium oleate solution. One milliliter of this solution contains 5×10^{-3} grams or 1.5×10^{-5} mol soap, and the total amount of soap solution spread on the surface contains, thereof, 1.68×10^{-7} mol soap, or about 1.0×10^{17} molecules ammonium oleate. Evaluating curve 1 of Figure 4 in the conventional way, one arrives at an extrapolated length of the compressed film of 28.2 centimeters. Multiplying this by the width of the tray (14.0 centimeters) one arrives at a spreading area A_s for the soap of 39.5 cm². This, divided by the number of soap molecules spread out on this area gives a surface requirement of 39.5Å² for a single ammonium oleate molecule, which compares with the figures found by N. K. Adam for potassium laurate (15).

Next, after the balance has been cleaned and readjusted, one spreads the same amount (0.0112-milliliter) of an emulsion, which was made up with a soap solution of the same concentration (0.5%), takes a compression curve with the emulsion, and determines the surface requirement A_e of the emulsion. It is, in all cases, less than that of the original soap solution. This indicates that the globules of the emulsion *together* with the soap left free after emulsification cover a smaller area than the original soap did. This is obvious because a considerable amount of soap has been used up to cover the surface of the emulsified particles. Let us assume we have n globular particles, all of them having the same radius r; then $n4\pi r^2$ is the total surface of the emulsified phase, and the amount of soap bound by adsorption on this surface will be proportional to it: namely, $\alpha n4\pi r^2$. The factor α takes into account that the density of the soap on a monomer particle may be different from the density of a soap layer on water. By comparing some of our results with direct optical observations, it seems, however, that under the conditions referred to in this article α was always in the neighborhood of unity. The soap contained in the original solution without monomer covers the area A_s; while the soap left free after emulsification of the monomer only covers A_e. Hence the difference $A_s - A_e = \Delta A$ must be made up by the soap, which is bound on the surface of the emulsified particles.

$$\Delta A = n\alpha 4\pi r^2 \qquad (D)$$

There are, however, the dispersed particles themselves which require a certain area on the surface of the trough, which will be proportional to their total cross-section $n\pi r^2$. This will therefore make it appear as if that much less soap has been adsorbed by the emulsified particles, and we therefore have to subtract it from the right side of equation (D). Hence one arrives at

$$\Delta A = n\pi r^2(4\alpha - 1)$$

The number n of the dispersed particles, on the other hand, can be expressed by the amount g of monomer in grams and by the density s as

$$n \cdot \frac{4\pi r^3}{3} s = g$$

$$n = \frac{3g}{4\pi r^3 s} \qquad (F)$$

Introducing (F) in (E) one finally arrives at

$$A = \frac{0.75(4\alpha - 1)g}{rs}$$

which permits the calculation of the particle radius from the experimentally determined value of ΔA by means of

$$r = 0.75(4\alpha - 1)\frac{g}{s\Delta A} \qquad (G)$$

A few remarks may be added for the use of this method. One requirement for a smooth operation of the hydrophil balance is to make all confining barriers of the spread systems nonwettable. We found that ferric-stearate is a very convenient and effective agent for this purpose. A solution of this material in benzene was spread on all confining surfaces of the films, and the benzene was allowed to evaporate. The surfaces were then wiped vigorously with a cloth to remove all excess of ferric-stearate, and only a very thin layer remained. The spreading of the pure soap solutions does not offer any difficulties, but the handling of the emulsions requires considerable care. Calibrated lengths of capillary tubing were used as micropipettes for the measurements of the volumes of the emulsions to be spread. One should not allow the unknown to drop into the water surface from any height, but place the orifice of the capillary immediately above the surface of the tray. Even then it happens that parts of the emulsion submerge and do not properly spread on the actual surface. This difficulty occurs frequently if already a considerable amount of polymer particles, the density of which is slightly larger than unity, has been formed, and if the emulsion does not contain mainly monomer as it does in the initial stages of the polymerization. Such cases have to be discarded, and another spreading attempt has to be made after the trough has been cleaned and refilled.

When a monomer emulsion was made up with a given soap solution, the initial particle size of it was determined by obtaining ΔA from two spreading measurements (pure soap solution and emulsion) carried out immediately one after the other. The particle sizes of the emulsions withdrawn during the polymerization were obtained by determining again ΔA from two spreading measurements, namely from the pure soap solution which was used to make up the initial emulsion and from the emulsion after polymerization had taken place to a certain extent.

Figure 4 shows four compression curves which have the usual shape and allow, with a reasonable degree of accuracy, extrapolation of the straight line part down to the abscissae. Curve 1 represents a soap solution and leads, as discussed above, to a satisfactory value for the surface requirement of a single ammonium oleate molecule. The other three curves reflect the behavior of three monostyrene emulsions and show that

smooth compression curves can be obtained with such systems. It may be noted that the linear (high pressure) portions of these curves are somewhat steeper than for the soap solution alone. As this was almost invariably observed with all emulsions, it seems to be no experimental error, but may reflect the fact that an emulsion containing particles of colloidal size is somewhat more difficult to compress than a soap solution. Table 4 shows the figures obtained with these three curves, and the approximate average particle radii derived from them under the assumption that both α and s in relation (G) are close to unity. In this case the equation reduces to

$$r = \frac{2.25g}{\Delta A} \qquad \text{(H)}$$

where g has to be measured in grams and ΔA in cm^2 in order to get r in cm. It can be seen that the average particle radii are in the range of microns as is to be expected for a system of the described properties.

Table 4. Average Particle Sizes and Other Characteristics of Several Samples

Average Particle Radii Derived According to Equation (A)

Width of the Trough, 14.0 Centimeters

Length of Soap Film in cm	Length of Emulsion Film in cm	ΔL in cm	ΔA in cm^2	g in Gram	$\bar{r}$	Curve No.
24.8	22.6	2.2	31	2.23×10^{-3}	1.6×10^{-4}	2
24.7	18.7	6.0	84	2.25×10^{-3}	0.6×10^{-4}	3
24.7	15.7	9.0	126	2.23×10^{-3}	0.4×10^{-4}	4

Using different amounts of soap, as indicated in Table 1, seven emulsions were made up from the same monomer, and their initial average particle radii were determined with the hydrophil balance. The results are given in Table 5, which also contains a number of other quantities of interest for the polymerization of such emulsions. In the first column there is the number of the emulsion which corresponds to that of Table 1; in the second, one finds the amount of soap used in mols. The third column contains the average particle radius, and the fourth the number of emulsified particles in the system; the fifth the total surface of the emulsified phase in one cm^3. In the sixth and seventh columns one finds the amount of soap adsorbed on the particle surfaces and the amount of soap which is still free (assuming that α is in the neighborhood of one). It can be seen from Table 5 that increase of the ratio soap to monomer leads to more highly dispersed systems, a fact which is well known from literature (11). This dependence of the average particle radius upon soap concentration is illustrated in Figure 5, where the average radii of the seven emulsions of Table 5 are plotted *versus* the soap concentration; one notes a very distinct decrease of particle size as the soap concentration increases.

Table 5. Data on Decrease of Particle Size with Increasing Soap Concentration

No. of Emulsions	Mols Soap Used	Particle Radius in $cm \times 10^{-4}$	Number of Emulsified Particles in System	Total Surface of the Emulsified Phase in cm^2	Mols of Soap Adsorbed	Mols of Soap Still Free
....	3.0×10^{-3}	3.6	1.1×10^{11}	1.5×10^{5}	1.0×10^{-4}	2.9×10^{-3}
....	3.3×10^{-3}	3.2	1.6×10^{11}	1.9×10^{5}	1.3×10^{-4}	3.2×10^{-3}
....	3.6×10^{-3}	2.6	2.8×10^{11}	2.3×10^{5}	1.5×10^{-4}	3.4×10^{-3}
....	4.0×10^{-3}	1.6	1.2×10^{12}	3.6×10^{5}	2.4×10^{-4}	3.8×10^{-3}
....	4.3×10^{-3}	1.4	1.8×10^{12}	4.3×10^{5}	3.0×10^{-4}	4.0×10^{-3}
....	4.6×10^{-3}	0.8	1.0×10^{13}	7.7×10^{5}	5.1×10^{-4}	4.1×10^{-3}
....	5.0×10^{-3}	0.4	8×10^{13}	1.5×10^{6}	1.0×10^{-3}	4.0×10^{-3}

Each of the emulsions was then polymerized in the presence of sodium perborate (compare Table 1) at 70° C. under moderate shaking in a number of equal ampules. At certain instances ampules were withdrawn, and the average particle size of the emulsion at that instance was determined by the above method. It must be pointed out that, as the polymerization proceeds, the emulsion becomes a more and more heterogeneous system. In the beginning there are only present soap solution and dissolved monomer particles. As the reaction proceeds, however, one has to consider soap solution, monomer particles, polymer particles, and the dispersed particles which consist of a solution of polymer in monomer or of polymer swollen in monomer. If one watches closely the spreading of emulsions, which contain already some polymer, it becomes evident that they are less homogeneous than the original monomer emulsion.

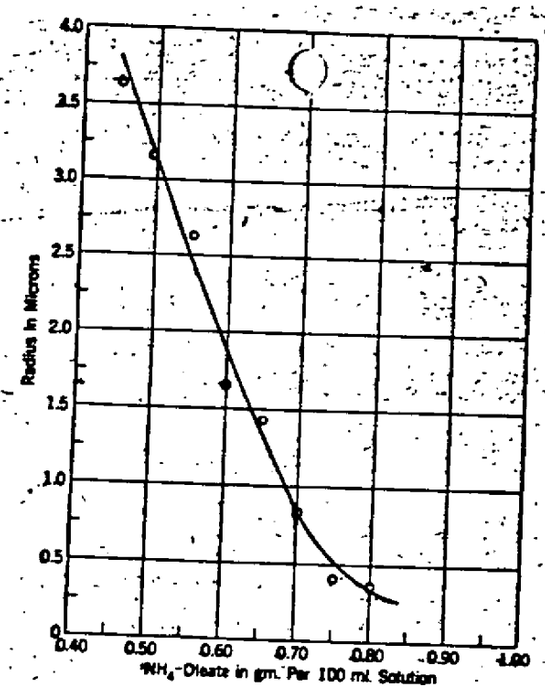


Fig. 5. Influence of Soap Concentration on the Average Particle Size

In all cases it was found that, as the polymerization proceeds, the average particle size of the emulsion decreases. Table 6 contains a few actually measured figures, and Figure 6 represents for several emulsions a plot of the average particle radius *versus* the time at which the sample was withdrawn. It can be seen that during the inhibition period the particle radius remains constant (in some instances even increases slightly); while it decreases sharply as soon as conversion of monomer into polymer sets in (compare the corresponding curves of Figures 1 and 6) and finally levels out at a figure much lower than the initial value.

Table 6. Average Particle Diameter of Samples (Containing Four Grams of Monomer) Withdrawn from Run No. 3 at Various Degrees of Conversion

Initial Particle Radius Is 2.6×10^{-4} Cm

Time of Polymerization in Hours	Weight of Polymer Formed in Grams	Degree of Conversion in %	Average Particle Radius in Microns
2.0	...	...	2.7
3.0	0.10	2.1	2.4
4.0	0.16	4.9	2.4
5.0	0.68	21.3	1.8
5.25	0.98	30.7	1.6
5.5	1.38	43.2	..
5.75	1.92	60.1	1.2
6.0	2.58	81.2	0.7
7.0	3.10	97.4	0.4

In order to find out whether this sharp decrease of the average particle size is directly connected with the chemical reaction in the system, we have run simultaneously samples taken from the same mother emulsion with and without catalyst under otherwise identical conditions, such as soap concentration, shaking, temperature, etc. Emulsions from ampules not containing any catalyst did not show any noticeable change in average particle radius. In fact if there were any significant change at all, it indicated a slight increase in particle size, due presumably to some agglomeration during the prolonged shaking. All emulsions, however, in which conversion of monomer to polymer took place exhibited a drastic drop in the average

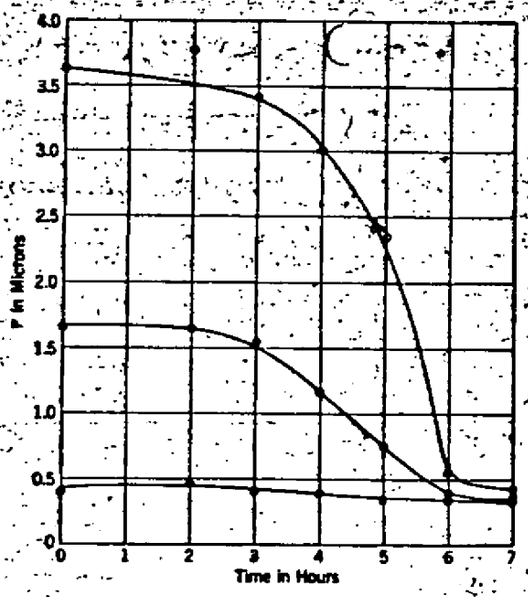


Fig. 6. Decrease of the Average Particle Size of Emulsions during Polymerization

particle radius, as indicated in Table 6 and Figure 6. In some cases the final average radius was as small as 500 Å (0.05-micron) although, in general, under the experimental conditions used in this study the final average particle radius was around 0.3-0.5-micron, and the ratio between initial and final radius about ten. This shows that at the end of the polymerization one has about a thousand times more particles present than at the beginning.

If one withdraws from one set of ampules two at a certain intermediate time (e.g., 5½ hours) and intermediate conversion (say 50%), measures the average particle size of one emulsion, adds an inhibitor to the other, and runs this one for another five or six hours, no additional conversion takes place, and no additional particle size drop has been observed, which shows again that particle size decrease is intimately connected with the chemical process of polymerization.

It seems that this experience together with the experimental results and ideas of Fryling, Vinograd, and their collaborators (3, 4) can be used to suggest qualitatively a mechanism for emulsion polymerization which localizes the different elementary steps, such as initiation, propagation, and termination of the growing chains outside of the *large* particles of the initial monomer emulsion. In the next article we shall try to advance such a mechanism and discuss it in the light of our general knowledge of polymerization processes.

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Bibliography

(1) W. P. Hohenstein, F. Vingiello and H. Mark, INDIA RUBBER WORLD, 110, 291 (1944).
(2) W. P. Hohenstein, S. Siggia and H. Mark, *Ibid.*, 111, 173 (1944).
(3) C. F. Fryling and E. W. Harrington, *Ind. Eng. Chem.*, 36, 114 (1944).
(4) J. R. Vinograd and collaborators, three lectures given at the A. C. S. meeting in New York, N. Y., September 13, 1944.
(5) V. Frilette, lecture given at the A. C. S. Meeting in New York, September 12, 1944.
(6) A. M. Sookne and Milton Harris, *J. Research Natl. Bur. of Standards*, 30, 1 (1943).
(7) A. R. Kemp and W. G. Straitiff, *Ind. Eng. Chem.*, 36, 707 (1944).
(8) M. L. Huggins, *J. Phys. Chem.*, 42, 911 (1938) and 43, 439 (1939); *J. Am. Chem. Soc.*, 64, 1712, 2716 (1942).
(9) P. J. Flory, *J. Am. Chem. Soc.*, 65, 372 (1943).
(10) T. Alfrey, A. Bartovics and H. Mark, *J. Am. Chem. Soc.*, 65, 2319 (1943).
(11) Compare the comprehensive books of: S. Berkman and G. Egloff, "Emulsions and Foams," Reinhold Publishing Corp., New York (1941); and W. Clayton, "Theory of Emulsions," Blakiston Co., Philadelphia (1943).
(12) R. T. Knapp, *Ind. Eng. Chem., Anal. Ed.*, 6, 66 (1934).
(13) Columbian Carbon Co., "Electron Microscope Study of Rubber Latices and Pigments," (1944).
(14) W. P. Davey, *J. Phys. Chem.*, 35, 115 (1931).
(15) E. Valko, "Kolloidchemische Grundlagen," p. 558, Julius Springer Co., Berlin (1937).

9-12-46

Methylation of Cane

1. Mix 32 gms. of cane + 150 cc of H_2O at 25°C
2. add 180 cc of 12.5% NaOH addition slowly, allowing the cane coagulate to a stiff jelly
3. Then immediately mix in 140 cc of 51% NaOH & 80 cc of $(Me)_2SO_4$ — the addition is intended over a period of 3 hrs. & adjusted so as to maintain alkaline conditions
4. The temp. is kept at 37°C & stirred vigorously during the reaction
5. The reaction is completed by heating at 100°C for 45 mins.
6. Cool to 18°C
7. add 50 cc of 95% alcohol
8. Pour into (6 vols.) ice cold water & allowed to stand for 24 hrs.
9. Filter out the ppted. NaOH (filter thru linen)
10. Continuously neutralized the filtrate with dil. H_2SO_4
11. Concentrate to a thick syrup.
12. Repeat the methylation second time

9-11-46

Saccharification of starch

G.P. 475,884 (L) 1921 L. Lilienfeld

G.P. 560,418 (L) 1924 L. Lilienfeld

J.A.C.S. 45, 1914 (1923) [illegible]

C.A. Tomkins & R. Adams J.A.C.S. 45, 2697 (1923)

C.A. 23, 5058 (1929)

B.P. 306,866 (L) 1928 J. G.

U.S.P. 1,850,828 1920 L. Lilienfeld

B.P. 181,595 (L) 1921 L. Lilienfeld

G.P. 497,240 1926 W. Hanns

G.P. 492,519 1926 J. G.

Monatsch. 49, 211 (1928) L. Ehrlich & M. Zeitler

Berichte 58A, 941 W. Philippi & K. Gerl
(Using T. Taka starch)

U.S.P. 2,116,363 1934 Du Pont

B.P. 520,625 Du Pont

Chem. Zbl. 1926, 1502-1503 L. Lilienfeld

RP 1951, 102 → Chem. Zbl. 1951, 8, 1362

(2) 9-11-46

Methylation of Starch, R. P. Wolf, Univ. of Iowa

1. a. C. S. 45, p. 2699-2701 C. G. Trimble & R. Adams
methyl starch!

Berichte 53, p. 1965-1968 L. Schmid
Cu-starch in textile with diazomethane

Comptes rendus, Académie des sciences, Vol. 177
p. 592-593 (1923)
H. Sautet
methoxy derivative of starch (1000 cited)

Biochemische Zeitschrift 248 p. 76-97 (1932)
P. A. A. J. C. Chowdhury
Starches are methylated by the action of dimethyl sulfate on the polysaccharides in the presence of 10% NaOH. In the case of starch 2 moles of acid were introduced for each glucose residue; the remaining unchanged groups were partially methylated by means of (Me)2SO4 & NaOH
C.A. 26 p. 640 (1932)

Dimethyl starch 32.7 $(C_6H_9O_5(OMe)_2)_n$
methylated starch 36.3
Trimethyl starch 43.7 $(C_6H_9O_2(OMe)_3)_n$

[illegible]

[illegible] NaOH [illegible] NH_4OH

[illegible]

[illegible] set-up

polystyrene – quick [illegible] into silicone [illegible]

1. Dispersing agents such as methylated starch

2. Protective Dispersing agents such as Polymethacrylic acid in alkaline medium

3. Cured rubber latexes

4. Pectinic acid dispersing agents

Disodyl Phthalate
&
Dicetyl-Cetyl Phthalate } are covered by Patents

To [illegible]

No 1

1. Investigation
   Warm R.W. start with pure
   Then H_2O

2. Various conducting agents
   1. Ideal case
   2. Impure
   3. Electrolyte
   4. Pure acids
   5. Impure acid

Criteria

A. 1. Test conductivity in normal
   Use a burette - H go into H_2O (or vice versa)
   Then no. 9

   Write to answer

D. Test for stability of conductivity

C. Use in small (very small) amounts

3.

EMULSION POLYMERIZATION OF ACRYLIC ESTERS

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Effects of various agents on the emulsion polymerization of acrylic esters are described, and directions are given for preparing several types of resin emulsions. When emulsion polymerization is used merely to convert monomeric acrylic esters into polymers or copolymers of relatively high molecular weight, Tergitol Penetrant No. 4 and ammonium persulfate can be used satisfactorily as emulsifier and polymerization catalyst, respectively. The resulting emulsion is only moderately stable and can be coagulated readily by the addition of aqueous solutions of sodium chloride, acetic acid, or mixtures of the two. Triton K60 and hydrogen peroxide also can be used conveniently to produce emulsions of only moderate stability. Emulsions remarkably stable to electrolytes (but not to mechanical agitation or solvents such as acetone and ethanol) can be made with Triton 720 as the emulsifier. Triton 720 and Tergitol Penetrant No. 4 can be used together in various proportions to produce emulsions of almost any desired stability to electrolytes. Stable emulsions suitable for brushing and spraying can be prepared with several combinations of agents. The combination used frequently for this purpose is E. F. Houghton No. 1, ammonium alginate, ammonium hydroxide, and ammonium persulfate. The viscosity of acrylic resin emulsions can be controlled over a wide range by using various quantities of ammonium alginate, modified casein, and Tergitol Penetrant No. 4. Films obtained from these emulsions adhere well to smooth surfaces.

BECAUSE of several inherent advantages, aqueous dispersions of resins, including the acrylic resins (*18*), are being used to an increasing extent for coating cloth, leather, and other materials. Advantages of aqueous dispersions include ease of application, rapid drying, and freedom from the fire and toxicity hazards that ordinarily accompany the use of resins dissolved in organic solvents.

During investigations in this laboratory concerned with the polymerization and copolymerization of acrylic esters and the production of stable resin emulsions, considerable information was obtained on the use of various emulsifiers and auxiliary agents in the emulsion polymerization of acrylic esters. Some of the results are given in the present paper. The first part of the paper describes various combinations of emulsifiers and polymerization catalysts for preparing acrylic resin emulsions of moderate or high stability; the latter part gives methods for preparing emulsions of almost any desired viscosity. The general properties, advantages, and applications of resin emulsions have been discussed at length elsewhere (*1, 5, 9, 10, 11, 19*).

The emulsions were prepared in a round-bottom, three-neck Pyrex flask fitted with glass-ground joints for a condenser, water-sealed glass stirrer, and thermometer well. Water and emulsifier were stirred and heated (below 85° C.) in the flask until a smooth dispersion or solution was obtained. The monomer or monomers were then added, and polymerization was induced by heat and catalysts. Hydrogen peroxide (30%) and ammonium persulfate were used as catalysts in many of the experiments. The emulsions were refluxed during the polymerization, and at refluxing temperature a period of 30 minutes to several hours was usually required. With half-moon or paddle-type stirrers operated at 100 to 150 revolutions per minute, emulsions with particle size as small as 0.05 micron in diameter were made without incorporation of air. The yield of polymer was almost quantitative. In some cases steam was blown through the emulsion at the end of the polymerization to remove unchanged monomer. The temperature rose during the polymerization from about 72° to 82° C. and from 85° to 92° C. when methyl acrylate and ethyl acrylate, respectively, were the monomers. Hence the course of the polymerization could be followed roughly by noting the temperature. The polymerizations were followed in some instances by observing changes in the refractive index, density, and solids content.

Emulsion polymerization can be carried out more satisfactorily if, in addition to suitable emulsifiers and catalysts, pure monomers and critical conditions of temperature and catalyst concentration are used. The monomer should be free of inhibitors or regulators or their amount and effect should be known. The monomer should be freshly distilled (under vacuum if high boiling) or, when storage is unavoidable, kept under conditions unfavorable for peroxide formation. Removal of inhibitor with dilute sodium hydroxide (1 or 2%) should be followed by several washings with distilled water, dilute sulfuric acid (0.01%), and twice again with distilled water. Removal of inhibitor from methyl and ethyl acrylate in this manner causes a considerable loss of monomer.

The amount of ammonium persulfate required to initiate polymerization depends largely on the temperature. Only traces of catalyst are needed under refluxing conditions (approximately 72° for methyl acrylate and 82° for ethyl acrylate), but much larger quantities are needed at somewhat lower temperatures. Polymerization may not occur in several hours with the same amount of catalyst if the temperature is as little as 0.5° below refluxing. Too much catalyst causes a vigorous reaction, violent refluxing, and, in some instances, coagulation of the emulsion. When only traces of catalyst are used at gentle refluxing temperature, polymerization proceeds smoothly, yielding a polymer of high molecular weight. Little or no additional heating is required, and the polymerization can be controlled by the rate of addition of the catalyst. A steam bath is more satisfactory than a water bath for this type of polymerization.

The benefits of carrying out the emulsion polymerization of monomers and monomer mixtures at refluxing temperature are so outstanding that some feature of refluxing other than temperature seems important. If it is assumed that most of the polymerization occurs in the aqueous phase, refluxing might be beneficial because of increased solubilization of the monomer or the increased rate at which the monomer is transported from the oil phase into and throughout the aqueous phase.

Fryling (*5*) described suitable laboratory methods for preparing resin emulsions from small quantities of monomers and for following the course of the polymerization.

EMULSIONS OF MODERATE STABILITY

The emulsifiers listed in Table I formed dispersions of moderate stability without auxiliary agents or other emulsifiers. Hydrogen peroxide (30%), which has the advantage of being essentially neutral and decomposing into water, was used conveniently as a catalyst in these initial experiments. In a few instances, when it

TABLE I. POLYMERIZATION OF METHYL ACRYLATE WITH ONE EMULSIFIER[a]

Expt. No.	Emulsifier: Trade Name	Emulsifier: Type (O, I)[b]	Grams	Water Ml.	Methyl Acrylate Ml.	H_2O_2 Ml.	Time Min.
1	Triton W-30	Sulfated aromatic ether alcohol	1.0	100	15	0.5	60
2	Triton K-60 S	Quaternary ammonium salt	1.0	100	15	0.5	60
3	Aerosol NR8F	Sodium alkyl aryl sulfonate	1.0	100	15	0.5	60
4	Gardinol LS	Fatty alcohol sulfate	1.0	100	15	0.5	60
5	Aquasol AR-75%	Sulfonated castor oil	1.0	100	15	0.5	60
6	Tergitol Penetrant No. 4	Sodium salt of higher secondary alkyl sulfate	1.0	100	15	0.5	60
7		Glyceryl monostearate	1.0	100	15	0.5	60
8	E. F. Houghton No. 1		1.0	100	15	0.5	60
9	E. F. Houghton No. 2		1.0	100	15	0.25	60
10	E. F. Houghton No. 3		1.0	100	15	0.5	60
11	Darad No. 11	Polymerized Na salts of alkyl naphthalene sulfonic acids	1.0	100	15	0.5	60
12	Darad No. 22	Polymerized Na salts of substituted benzene alkyl sulfonic acids	1.0	100	15	0.5	60
13	Atlas Span 85	Sorbitan trioleate	1.0	100	15	0.5	60
	Atlas Tween 85	Sorbitan trioleate polyoxyalkylene derivative	1.0	100	15	0.5	60
14	Atlas Span 20	Sorbitan monolaurate	1.0	100	15	0.5	60
	Atlas Tween 20	Sorbitan monolaurate polyoxyalkylene derivative	1.0	100	15	0.5	60
15	Emulphor EL-719	Ethylene oxide condensate with fatty acids	1.0	100	15	0.5	60
16	Emulphor ON-870		1.0	100	15	0.5	60
17	Igepon T	$C_{17}H_{33}CON(CH_3)CH_2CH_2SO_3Na$	1.0	100	15	0.5	60
18	Igepon AP extra	Na sulfonate of oleic acid ester of isethionic compound	1.0	100	15	0.5	60
19	Nekal BX	Sodium alkyl naphthalene sulfonate	1.0	100	15	0.5	60
20	Nekal BX	Sodium alkyl naphthalene sulfonate	1.0	100	15	0.5	60
21	NH_4 Alginate	Ammonium alginate	1.0	100	15	0.5	60
22	Pectinate H-69	Acid-demethylated pectin	1.0	100	15	0.5	60
23	Protovac 8979	Modified casein	1.0	100	15	0.5	60
24	Nekal A	Sodium alkyl naphthalene sulfonate	1.0	100	15	0.5	60

[a] The mixture was reflux (temperature of mixture, 75° C.) until polymerization was virtually complete.
[b] A large amount of polymer separated during the polymerization.
[c] Emulsions were satisfactory except for brushing or spraying.
[d] 0.5 gram benzoyl peroxide was also used.
[e] Heating reduced emulsifying action.
[f] A small amount of polymer separated during polymerization.

appeared that hydrogen peroxide alone was not sufficiently effective, a small amount of benzoyl peroxide was added. Ammonium hydroxide, Houghton No. 2, Triton NE, Emulphor AG, and Nekal RU appeared to inhibit the polymerization of methyl acrylate under conditions similar to those shown in Table I.

The emulsions obtained with single emulsifiers (Table I) were not stable enough for brushing or spraying. Optimum conditions for each emulsifier were not determined, and it is possible that different concentrations and conditions would have given improved emulsions. Emulsions of only moderate stability are desirable for some purposes, and some of the formulas of Table I could be used to advantage under such circumstances. Triton K60S (experiment 2) has been used conveniently in this laboratory many times in converting acrylic esters into resins of relatively high molecular weight; in these experiments the emulsions were coagulated by the addition of dilute solutions of sodium chloride, acetic acid, or mixtures of the two.

When used under the conditions shown in Table I, the following materials appeared unsuitable as emulsifiers in the polymerization of methyl acrylate: Triton W-30, Gardinol LS, glyceryl monostearate, Houghton No. 3, Darad No. 11, Atlas Span 85 + Atlas Tween 85, Atlas Span 20 + Atlas Tween 20, Igepon AP extra, ammonium alginate, Pectinate H-69, Protovac 8979, and Nekal A. These agents were not studied thoroughly, however, and excellent results might have been obtained with other monomers under other conditions, or when used in conjunction with other emulsifiers.

STABLE EMULSIONS

Some of the emulsifiers that had given promising results in the earlier experiments (Table I) were used in later experiments with other agents. Emulsions stable enough for brushing and spraying were obtained with certain combinations of agents (Table II). It was not demonstrated that these combinations would function satisfactorily with all monomers, but stable emulsions were obtained when methyl acrylate was polymerized alone or copolymerized with acrylonitrile or bis-(carballyloxyethyl)maleate (prepared from 2 moles of allyl lactate and 1 mole of maleic anhydride). The combination used most often consisted of Houghton No. 1, ammonium alginate, and ammonium hydroxide (experiments 1 to 5 and 18 to 23, Table II, and experiment 6, Table IV). Ammonium hydroxide had little or no inhibiting effect, possibly because it was partly or totally neutralized by Houghton No. 1.

Triton 720 (sodium salt of aryl alkyl polyether sulfonate) formed emulsions that were remarkably stable to electrolytes (Table III). Although stable when treated with sodium chloride, acetic acid, or hydrochloric acid, the Triton 720 emulsions could be coagulated by mechanical treatment or by the addition of alcohol or acetone. With mixtures of Triton 720 and Tergitol Penetrant No. 4, emulsions of almost any desired stability to electrolytes were prepared (Table III).

SELECTION OF POLYMERIZATION CATALYST

Although hydrogen peroxide has certain advantages and was used satisfactorily in many experiments, the ammonium persulfate is preferable as catalyst. With this agent the polymerizations proceeded smoothly, and it was effective in exceedingly low concentrations. Polymers of high molecular weight could be prepared easily with traces of it. Presumably potassium and certain other persulfates could be used. Sodium perborate appeared to have no particular advantage. Benzoyl peroxide was active and was used in conjunction with hydrogen peroxide when the latter proved ineffective.

Ammonium persulfate was not employed with all the emulsifiers shown in Tables I and II, but it was used satisfactorily with Tergitol Penetrant No. 4 and a mixture of Houghton No. 1, ammonium alginate, and ammonium hydroxide. Other examples of the preparation of satisfactory emulsions with ammonium persulfate are given in Tables III and IV. Unlike hydrogen peroxide, ammonium persulfate was unsatisfactory with Triton K60, owing to the formation of a precipitate.

MISCELLANEOUS OBSERVATIONS

Of the several agents tried (mineral oil, n-octanol, lauryl alcohol, n-hexanol, castor oil, and ethanol), n-octanol and n-hexanol seemed most suitable for preventing foaming. A small amount was added during the polymerization when foaming became excessive.

Dodecyl mercaptan appeared to facilitate control of the rate of polymerization, particularly when hydrogen peroxide was used as catalyst.

The effect of pH was not studied thoroughly, and few conclusions were reached regarding the desirability of controlling this

[a] Obtained through the courtesy of L. T. Eaton of E. F. Houghton & Company.

variable. Fryling (6) made interesting observations regarding changes in pH during emulsion polymerization.

Use of extremely small quantities of emulsifiers was not studied, but polymerization occurred less readily when Triton K60 was used in low concentration with hydrogen peroxide as catalyst. This is in agreement with the observations of Fryling (6).

Unless monomers (usually about 2% of the quantity used in the experiment) were removed, the emulsions had an objectionable odor. In many instances, steam was passed through the emulsions at the end of polymerization to remove residual monomers and improve the odor.

CONTROL OF VISCOSITY

Viscosity influences the ease with which both resin emulsions and solutions can be applied. The viscosity of resin solutions increases so rapidly with increase in resin concentration that the resin content must be kept low enough for convenient application. On the other hand, aqueous resin dispersions usually are fluid, even when the resin content is 50% or even higher. Data supplied by Jackson (8) illustrate the differences between the viscosities of aqueous dispersions and ethyl acetate solutions of an acrylic resin (Table V).

The viscosity of resin solutions can be controlled easily by changing the resin concentration (Table V) or the solvent, but the viscosity of resin emulsions cannot be controlled by these methods. Since resin emulsions are ordinarily fluid, several agents, including methylcellulose (1), have been added to increase the viscosity and facilitate brushing, spraying, or calendering (7). Although these agents are useful for some purposes, some of them have distinct disadvantages. Methylcellulose, for example, cannot be added before polymerization because its solutions are coagulated by elevated temperatures. Moreover, it is moderately soluble in cold water, and films containing methylcellulose would be expected to have decreased water resistance.

During this study a simple and effective method for preparing acrylic resin emulsions of almost any desired viscosity was found. This consists in adding a casein preparation and a water-soluble alginate before polymerization. The casein and alginate have a synergistic effect on

Figure 1. Electron Micrographs of Methyl Acrylate Polymer Emulsions

viscosity, and small amounts of these two agents, when used together, produce highly viscous emulsions.

The emulsions were made with the equipment and technique described early in the paper. After polymerization was completed, the emulsions were allowed to cool to room temperature with stirring and were then poured into glass bottles to stand overnight before the viscosity was measured. The samples were shaken gently, and the viscosity was determined with a Brookfield Synchro-lectric viscometer at 6, 12, 30, and 60 revolutions per minute. The emulsions were thixotropic and, in some instances, considerably thinned by agitation. The accuracy of the viscometer was checked periodically with oils of known viscosity supplied by the National Bureau of Standards. No attempt was made to maintain an accuracy higher than 10% of the scale value of the instrument.

It has been claimed (*) that casein retards the polymerization of some monomers. Results of the present work indicate that this effect causes no real difficulty. Of the various casein preparations studied—Protovac 8979, rennet casein, and acid casein—satisfactory results were obtained only with Protovac 8979.

Although emulsifiers other than Tergitol Penetrant No. 4 were given little attention, Triton K60 and Daxad No. 11 were used satisfactorily (in combination with ammonium alginate and modified casein) to produce viscous acrylic resin emulsions. Nacconol seemed less suitable.

The few observations made of the pH value indicated that the emulsions were never highly acidic or basic. This might have been partly due to a buffer-like action of the casein. In some instances a mixture of sodium borate and sodium hydroxide was added before polymerization without any important noticeable effect.

The size of resin particles in several methyl acrylate polymer emulsions was determined by examination of electron micrographs. Representative fields are shown in Figure 1. The particle size in some emulsions was rather uniform, most diameters lying in the range 0.1 to 0.4 micron (Figure 1A). B illustrates the aggregation of spherical particles of the same emulsion to form chains, clusters, and networks. In many cases coalescence was incomplete, as evidenced by density variation over the image of aggregates and especially by the circular outline of particles near the periphery. C shows the tremendous variability in particle size in one of the resin emulsions. Particles ranged from less than 0.1 to more than 7 microns in diameter.

Films were prepared from some of the emulsions (casein and ammonium alginate type) by spreading the emulsion on a pane of glass and allowing the water to evaporate. The films prepared from foamy emulsions had bubbles, but this difficulty could be avoided by adding a small amount of n-butanol or n-octanol, either before or after the emulsion polymerization. Because of

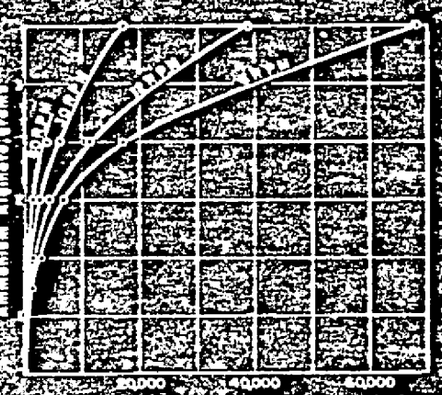


Figure 2. Effect of Ammonium Alginate on Viscosity

TABLE III. EMULSION POLYMERIZATION OF ETHYL ACRYLATE

Expt. No.	Emulsifier	Grams	Water Ml.	Ethyl Acrylate Grams	Ammonium Persulfate Mg.	Time Min.
1	Tergitol Penetrant No. 4	8	900	200	8.0	30
2	Tergitol Penetrant No. 4 paste	8	400	200	8.0	50
3	Triton 720	2.5	400	180	8.0	50
4	Triton 720	1.0	400	200	8.0	60
	Tergitol Penetrant No. 4	4.0				
5	Triton 720	4.0	1600	400	8.0	100
	Tergitol Penetrant No. 4	14.0				
6	Triton 720	10.0	4000	2000	40.0	180
	Tergitol Penetrant No. 4 paste	60.0				

[a] Reduced, temperature 82-91° C.

TABLE IV. EMULSION POLYMERIZATION OF METHYL ACRYLATE

Expt. No.	Ammonium Alginate Grams	Protovac 8979 Grams	Other Agents, Grams	Water Ml.	Methyl Acrylate Grams	Ammonium Hydroxide Mg. O	Ammonium Persulfate Mg. O	Time Hr.
1	1.25	10.0	Tergitol Penetrant No. 4 8.0	300	150	0.1	0.125	1½
2	1.25	33.0	Tergitol Penetrant No. 4 13.6	1500	750	10.0	0.115	1½
3	4	8.0	Tergitol Penetrant No. 4 8.2	340	175	0.1	0.125	1½
4	1.4		T-Ascorbopalmitate, 1.0	175	115	1.0	0.150	1½
5	1.4		Citric acid, 1.5; Pectinate B-69,[d] 1.0	300	150	1.0	[e]	[e]
6	1.0		S. F. Houghton No. 1, 1.0	250	250	5.0	0.600	1½

[a] 15 ml. n-butyl alcohol also used.
[b] 0.3 g. Sudan Red BBA dissolved in monomer.
[c] Palmitate of ascorbic acid (14).
[d] 12 ml. H_2O_2.
[e] Apple pectin after demethylation with acid.

TABLE V. VISCOSITIES OF COMPARABLE SOLUTIONS AND EMULSIONS OF POLYMERIZED ETHYL ACRYLATE

Concn. of Former, %	Viscosity, Minutes: Ethyl acetate soln.	Aqueous dispersion
5	17.2	12.2
10	64.6	12.4
20	No longer measurable	12.7
25	Ditto	12.8
40	Ditto	20.3

Viscosities were determined at 20° C. in the No. 4 Ford cup.

TABLE VI. EFFECT OF AMMONIUM ALGINATE ON VISCOSITY OF METHYL ACRYLATE EMULSIONS

Expt. No.	Ammonium Alginate, Grams	Brookfield Viscosity, Centipoises: 5 r.p.m.	10 r.p.m.	20 r.p.m.	50 r.p.m.
1	0.25	Too low	Too low	6	6
2	0.75	40	40	35	32
3	1.25	910	1,015	870	760
4	1.75	3,600	2,350	1,200	780
5	2.00	6,400	4,150	2,200	1,440
6	2.50	17,000	10,800	4,600	2,750
7	3.50	48,000	39,000	17,200	Above range of minds

Ingredients other than ammonium alginate: water, 350 ml.; Protovac 8979, 7.5; Tergitol Penetrant No. 4, 3 g.; methyl acrylate, 250 ml.; dodecyl mercaptan, 1 ml., and hydrogen peroxide. Viscosity of water at 20° C. is 1.0050 centipoises.

excellent adherence, it was difficult to remove some of the films from the glass surface. The films could be removed easily, however, after soaking in hot water.

Water resistance of some of the films was determined by suspending a strip of the film in water for several days, noting the increase in weight, and observing the effect of the water on the appearance and strength of the specimen. Resistance to water was not satisfactory, but the methyl acrylate and methyl acrylate-acrylonitrile films were little affected by hydrocarbons containing less than 50% aromatics.

EFFECT OF AMMONIUM ALGINATE. As mentioned above, the greatest increase in viscosity resulted when both the alginate (Superloid) and casein preparation (Protovac 8979) were used. Increasing the proportion of alginate, however, was more effective in increasing the viscosity than using larger amounts of the modified casein (Table VI and Figure 2). When the quantity of ammonium alginate was increased from 0.25 to 3.5 grams, the viscosity of the resulting emulsions was raised from approximately 2 to 68,000 centipoises, a 34,000-fold increase. This remarkable increase in viscosity, however, depended on the modified casein, since fluid emulsions (2 to 3 centipoises) resulted when the casein preparation was omitted. It is apparent from Figure 2 that the greatest effect on the viscosity was caused by increasing the quantity of ammonium alginate from 2 to 3.5 grams (0.84 to 1.47% by weight of the methyl acrylate polymerized).

EFFECT OF MODIFIED CASEIN. The modified casein (Protovac 8979) also increased the viscosity of the emulsions (Figure 3).

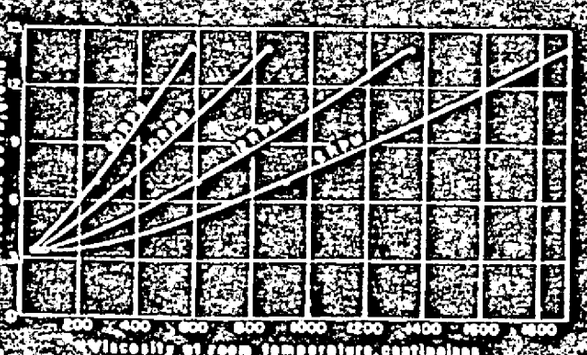


Figure 3. Effect of Protovac 8979 on Viscosity

Less than approximately 3 grams had little effect on the viscosity, but the viscosity increased greatly when the quantity was increased from 3.5 to 14 grams (1.47 to 5.9% by weight of the methyl acrylate polymerized).

The quantity of the casein preparation required to produce viscous emulsions was appreciable; hence the influence of the casein on the properties of the resin films deposited from the emulsions merits consideration. The films obtained from the resin emulsions contained approximately 1.5 to 6.0% of the modified casein. The casein decreased tack and increased the water resistance of the films but the most noticeable effect was the increased tenacity with which these films adhered to smooth surfaces. Hence, the overall effect of the casein preparation in the resin film appears beneficial. Butler (3) stated that as much as 10% of Protovac 8979 in films of ester resin does not affect water resistance or durability.

Figure 4. Effect of Resin Content on Viscosity of Polymethyl Acrylate Emulsions (Brookfield)

EFFECT OF RESIN CONCENTRATION. Unlike the acrylic resin emulsion (Table V) described by Jackson (8), the viscosity of the emulsions prepared with peptized casein and ammonium alginate was dependent on the resin content, particularly when the resin content was higher than 15% (Figure 4). This fact may be attributed to the alginate and modified casein, since emulsions containing as much as 55% of acrylic resins were fluid in the absence of these agents. Other ingredients used in the experiments shown in Figure 4 were 150 ml. water, 0.4 gram ammonium alginate, 3.0 grams Protovac 8979, 1.2 grams Tergitol Penetrant No. 4, and hydrogen peroxide.

ACKNOWLEDGMENT

The section microscopic examination was made by F. R. Senti and G. C. Nutting of the Analytical and Physical Chemistry Division of this laboratory.

LITERATURE CITED

(1) Anonymous, *Brit. Plastics*, 15 (171), 168–70 (Aug., 1943).
(2) Barron, H., *Ibid.*, 11, 404–7 (April, 1940).
(3) Butler, W. H., *Paint, Oil Chem. Rev.*, 105, No. 1, 10–14 (1943).
(4) Clayton, W., "Theory of Emulsions and Their Technical Treatment," 4th ed., Philadelphia: Blakiston Co., 1943.
(5) Fryling, C. F., Ind. Eng. Chem., Anal. Ed., 16, 1–4 (1944).
(6) Fryling, C. F., and Harrington, E. W., Ind. Eng. Chem., 35, 1114–17 (1943).
(7) *India Rubber World*, "Compounding Ingredients for Rubber," Bill Brothers Pub. Corp., 1936.
(8) Jackson, C. M., *Brit. Plastics*, 14 (166), 377–82 (1943).
(9) Mattiello, J. J., "Protective and Decorative Coatings," Vol. IV, New York: John Wiley & Sons, 1944.
(10) Nassaro, R. T., *India Rubber World*, 106, 345–6 (July, 1942).
(11) Nassaro, R. T., *Paper Trade J.*, 115, 29–32 (Nov., 1942).
(12) Neher, H. T., Ind. Eng. Chem., 28, 267–71 (1936).
(13) Renfrew, A., and Flint, C. F., *J. of Chemist.*, 19 (210), 194–8 (1943).
(14) Sayre, D., Blirton, A. J., Turer, J., and Wells, P. A., Oil & Soap, 20 (11), 224–6 (1943).
(15) Van Antwerpen, F. J., Ind. Eng. Chem., 35, 1–6, 30 (1943).

U. S. 2,163,305 June 20, 1939 H.R. Dittmar (du Pont)

Methyl or ethyl starch used as emulsifying agent and, subsequent to polymerization, hyrolysing the starch or starch ether by the action of pancreatin, amylopsin, pancreatic amylase. The starch is converted to glucose, or other deratives which can be washed off with water.

Example 3 (a)

A glass-lined jacketed kettle of 50 gal capacity provided with stirrer and reflux condenser was charged with 25 gal of water and 5 gal of monomer containing 1% of benzoyl peroxide and 0.8 of 1% of methyl starch containing 0.05 methyl groups per $C_6H_{10}O_5$ group. Stirred at 550 rpm at 80° for 1 hour. The granular polymer washed with distilled water.

The powder was molded at 170° and 3000 lb/in^2. Disc hazy due to residual methyl starch.

Example 3 (b)

Same as above; but prior to washing, the powder was subjected to the enzymatic hydrolysis of 0.02% of pancreatin (based on polymer) for 15 min at 40°C.

Molded as above; brilliantly clear and transparent article. Much stronger molded article than in 3 (a).

Pancreatin — Will Corp.
Methyl starch —

U. S. 2,201,395 May 21, 1940 R. A. Fletcher (du Pont)

Example 1

Mixture A:	Methyl methacrylate	900 parts
	α-Terpineol	80 "
	"C-18 alcohol"	20 "
	Benzoyl peroxide	7.2 "

C-18 alc (a mold lubricant) is a mixture of alcohols from hydrogenated esters of cocoanut oil.

Mixture B:	Distilled water	1,950 parts
	Disodium acid phosphate	7.6 "
	Monosodium " "	0.4 "
	Polymethacrylic acid	1.0 "
	Sodium hydroxide	0.46 "

The mixtures of A and B are combined and agitated rapidly while being heated to a temp of 80°C. Refluxed for about an hour. Polymer tiny beads.

Example 2

Mixture A:	Methyl methacrylate	1,520 parts
	α-Terpineol	180 "
	Benzoyl peroxide	15.2 "
Mixture B:	Distilled water	2,250 "
	"Gardinol"	18.75

"Gardinol" (as emulsifying agent) is sodium salts of higher fatty sulfate esters.

The mixture of A and B are combined and passed through a colloid mill, to effect emulsification. It is heated to 75 - 80° until polymerized. The polymethyl methacrylate is recovered from the emulsion, and the resin compacted into form suitable for injection molding.

Example 4

Mixture A:	Methyl methacrylate	97
	Terpineol	3
	"Loral" (lubricant)	2
	Benzoyl peroxide	1
Mixture B:	Distilled water	200
	Disodium acid phosphate	1
	Mono " "	0.05
	Polymethacrylic acid	0.6
	NaOH	0.3

Terpineol - Will Corp.

"Duponol ME", a commercial preparation of sulfated fatty alcohols, is also used as emulsifying agent.

U. S. 2,244,702 June 10, 1941 L. P. Kabbuch (du Pont)

Example 1

Mixture A:	Distilled water	3,834	parts
	1% aq. solution of methyl starch	166	"
Mixture B:	80% methyl methacrylate, 20% methacrylic acid	1,960	"
	Straight chain aliphatic alcs(c-18)	40	"
	Benzoyl peroxide	15.7	"

The combined liquids were introduced into a vessel equipped with a reflux condenser and an anchor agitator and were stirred by the agitator at 850 rpm. While being heated to the refluxing temp of 82°C. After 30 min of refluxing, the monomer was polymerized to very small solid globules. The liquid is decanted, the powder is washed three times in distilled water and dried at 70° for 20 hours.

The softening point of the molded product increases with the increasing proportion of methacrylic acid.

Example 3

A solution of 475 parts of methyl methacrylate, 25 parts of methacrylic acid, and 5 parts of benzoyl peroxide added to a solution of 1.5 parts of methyl starch in 1000 parts of water, at 70°, while stirring. After the addition of the mixed monomers, the temp of the monomer-water dispersion was rapidly increased to its refluxing temp (82°). The temp rose to 95°C.

The fine white granules which were washed thoroughly with water and dried for 16 hours at 80°C. Yield = 483 parts.

Compression molding at 170° and 2000 lb/in^2 gave a transparent and tough disc.

U. S. 2,265,242 M. Marks (du Pont)

Polymethacrylic acid as a granulating agent is in part strongly adsorbed upon the granules of polymer and tends to impair the transparency of the resin, and promotes discoloration by heat.

Detergents are likely to produce haze.

Example 1

Methyl methacrylate	100 g
Benzoyl peroxide	1
Distilled water	350
Buffer solution	10
Polymethacrylic acid	1

The buffer solution contains:

Disodium acid phosphate	1.71
Monosodium " "	.09
Balance: distilled water	

The benzoyl peroxide is dissolved in the methyl methacrylate, and the resulting solution is filtered. The polymethacrylic acid is dissolved in the water and buffer solution is added. The resulting solution is filtered. The pH is about 7.5

The mixture is heated to 80-82°C in a kettle with stirrer and reflux condenser. Polymerization comleted in about 45 min.

The polymer is agitated with a large volume of aqueous solution of sodium hexamethaphosphate (0.5%) at 70° for 5 minutes. The granules are washed and dried.

Example 2

The filtrate from example 1 is about 360 ml. Some of this is used as a granulating agent in this example.

Methyl methacrylate	100 g
Benzoyl peroxide	1 g
Filtrate from example 1	180 ml
Distilled water	175 g
Buffer solution	5 g

The operation is same as in example (1).

Br 457,284 Oct 28, 1935 du Pont

A solution prepared of methyl methacrylate, water, and methanol, the proportions being such as to correspond to cloud point conditons.

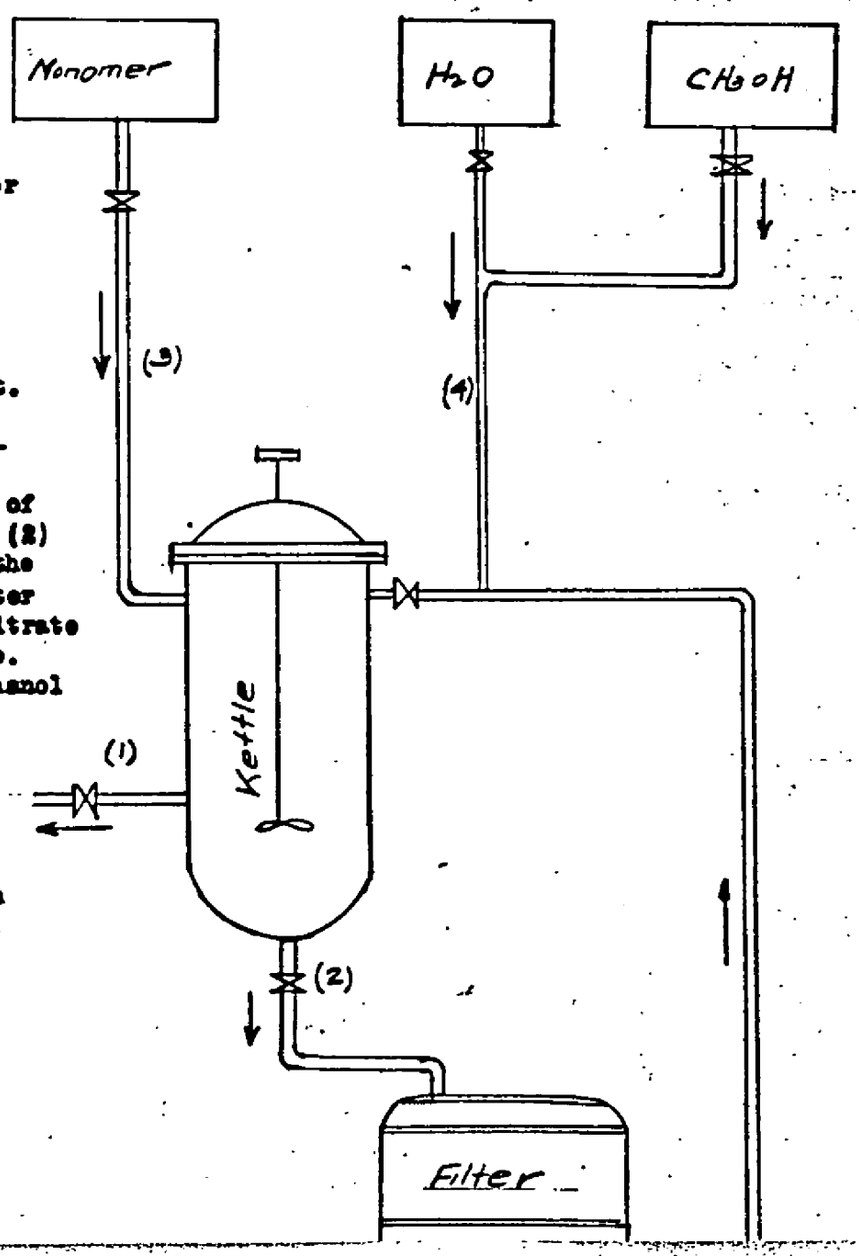
The process is effected in a closed and steam jacketed kettle provided with two valved inlets (3) and (4). Inlet (3) serves for the introduction of monomer from a stock tank and the inlet for the introduction of polymerization medium (water and alc.).

Example:
Into this vessel is introduced a mixture of 10 parts by vol MeMe, 40 parts CH_3OH 50 parts of water.

The mixture is gradually heated to 65°C, with stirring, samples being taken at frequent intervals, through the sampling outlet (1) to determine when separation of polymer has begun. When sepn. is observed, addition of fresh monomer is begun and continued thereafter so as to maintain the the mixture in the kettle at the cloud point.

When substantial polymerization has taken place (but still being capable of being circulated), valve (2) is partially opened and the product withdrawn to filter (or centrifuge). The filtrate is returned to the kettle. Additional water and methanol are let in as required.

The polymer is washed with methanol, dried for 3 hrs. at 20°C and 3 hrs. at 120 - 140°C. The granular material can be broken up or powdered.



U. S. 2,133,257 Oct 11, 1939 D. E. Strain (du Pont)

Example 3

562 parts of a 5% aq. solution of water soluble polymethacrylamide were freed from suspended insoluble matter by centrifuging and were then diluted with 5000 parts of water. This solution was added to 2270 parts of methyl methacrylate monomer containing 22.7 parts of benzoyl peroxide, and the mixture was placed in an enameled cast iron jacketed vessel fitted with reflux condenser and a mechanical stirrer with a water seal. Heated to 80°C.

When the bulk of the reaction had taken place, the vessel was heated through a steam jacket and the temp of the reaction raised to 90° to complete the reaction.

The solid product is separated by decantation and centrifuging, and dried at 90°C, giving a white sand-like powder, which upon molding at 150-180° and 4000 lb/in^2, gives a product of high strength.

Example 4.

One volume of methyl methacrylate and 2 volumes of 28-29% aqua NH_3 was allowed to stand with periodic shaking for 2-3 days at room temperature. This was distilled to half the volume at 100-125 mm. Water distilled off was replaced by distilled water, and pH lowered to 5.0 by glacial acetic acid. The solution then was placed in an oven at 60°C for 3-5 days. A thick gel-like resin resulted.

Example 5

A glass-lined jacketed kettle of 50 gal capacity provided with a stirrer and a reflux condenser was charged with 25 gal of water and 5 gal of methyl methacrylate containing 1% of benzoyl peroxide and 0.8 of 1% of the gel-like

U. S. 2,171,765 Sept 5, 1940 Rohm & Haas

Example

200 parts of a colloidal suspension of aluminim hydroxide containing 2 gm Al_2O_3 per liter is heated to 95°C. A mixture of 40 parts of methyl methacrylate with 60 parts of butyl acrylate containing 0.5% of benzoyl peroxide is added slowly while stirring.

The polymerization is complete after two hours and the polymer is in the form of glass-clear beads which may be feed of any adhering aluminum hydroxide by washing with water.

Fine powders of methyl methacrylate, talc (5%), barium sulfate, aluminum oxide, and ferric oxide may also be used.

The size of granules depends on the rate of addition of the monomer (usually ½ hr), and on the powder used in dispersion.

Ethoxy-methylen-malonsäure-diäthylester

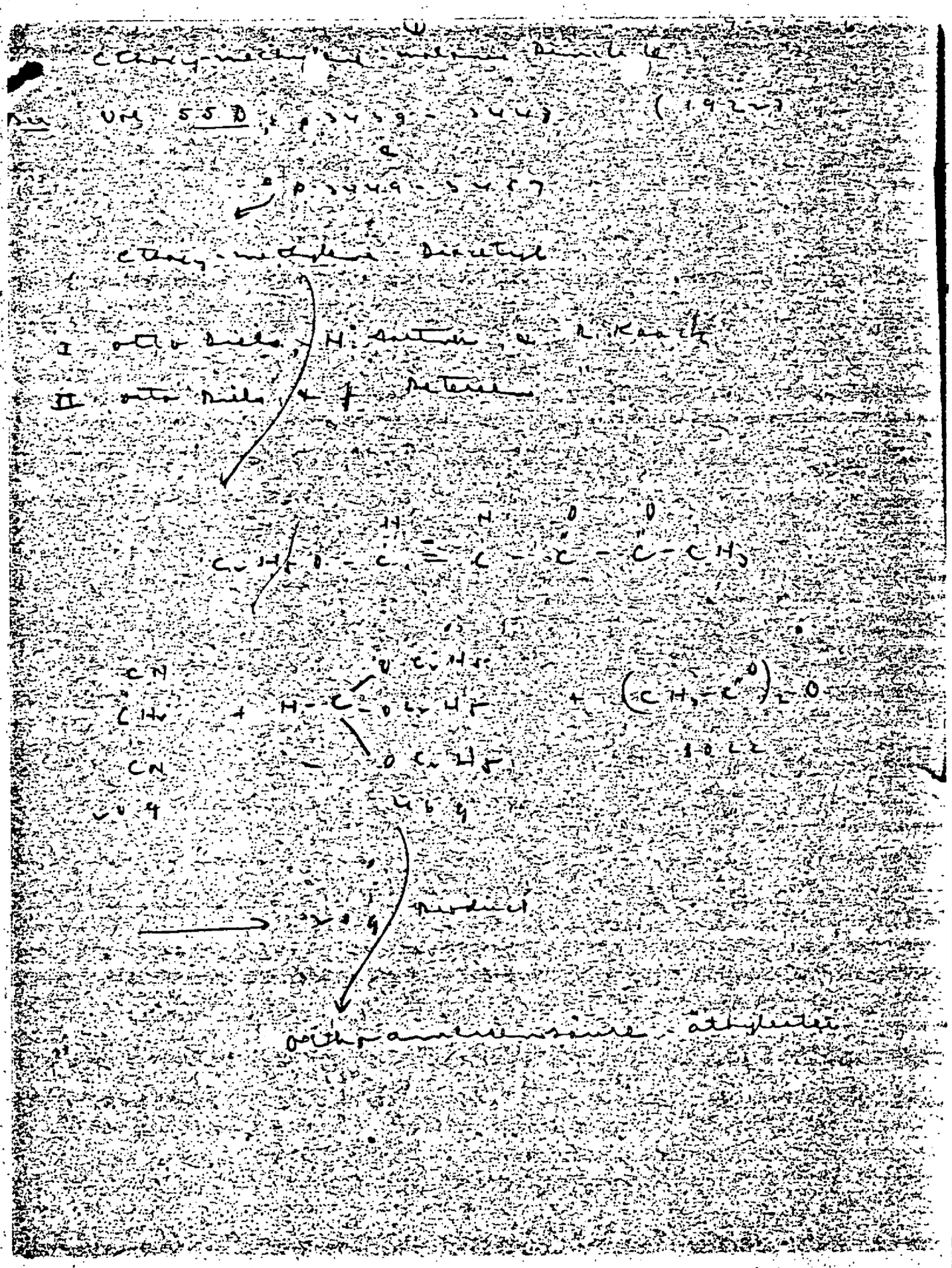
Ber. 55 B, p. 3439–3447 (1922)

p. 3443–3447

Ethoxy-methylen-diäthylester

I. oxo-diäthyl, H. Anton & R. Kaatz

II. oxo-diäthyl & f. Petersen



[illegible]

[illegible] (not under 60°C)

15. The aqueous alcoholic [illegible] of the product is [illegible] to dryness, [illegible] redissolved in water and treated with CHCl3 (a small excess of boiling water CHCl3)

16. The solution is concentrated [illegible] a third material extracted by CHCl3 [illegible] the methylated stand and then after the methylated stand is completely soluble in aqueous alcohol & in [illegible] insoluble by [illegible] water.

17. The solution of the product by [illegible] with CHCl3 is carried out as already described. Difficulties may be experienced [illegible] filtering the CHCl3 solution by ordinary methods as the methylated [illegible] form continuous films [illegible] filter paper.

18. On removal of the solvent, a stiff [illegible] remains which is [illegible] completely to a white powder. A similar [illegible] (red water) [illegible] in [illegible] CHCl3 & is [illegible]

Vol. No. 6 P. 9-12-46

1. The product is boiled with a mixture of MeI to which MeOH is gradually added till the solid becomes completely clear.

2. 1.4 g AgNO3 are added in small portions to the mixt. kept at the b.p. for 1 hr. Nothing EtOH is added as the intermediate, the further solvent being dried against, the further solvent being dried in the same way as EtOH (dried) to the mixture in EtOH (dried).

3. The mixture is refluxed 6 hrs on a water bath.

4. Finally the methylation is carried out by boiling with C6H6 (allowing EtOH vapor to escape the end-time using a suitable sep. funnel separator).

5. Convert the methylation product into acid by saponification.

[illegible] — m.p. [illegible]
[illegible] — m.p. 110° (from [illegible])
[illegible] m 0.95 b

d-arabinose — m.p. 164.5°

1-N-nitrosamino-4,5-dimethylbenzene — m.p. 142°C
and MeOH → yellow

Step 4

1-N-nitrosamino-2-arabitol-4,5-dimethylbenzene
for boiling EtOH — and dil. EtOH for recrystallization

Step 5

1-N-nitrosamino-2-amino-4,5-dimethylbenzene

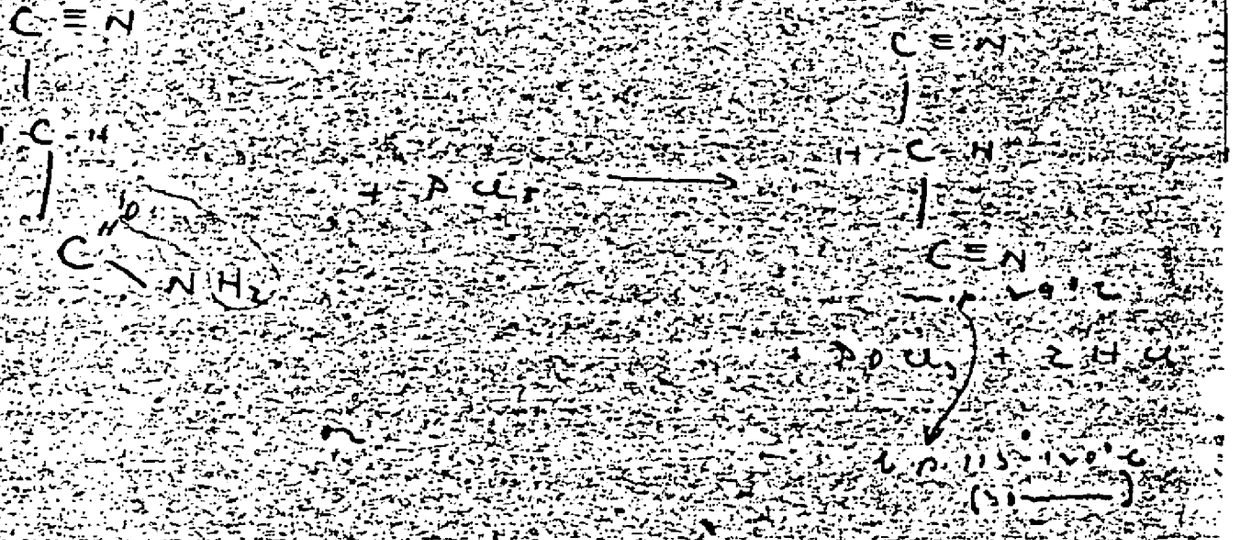
Riboflavine — 91.2°C

Condition of dimethylglycine solution { H-D, EtOH

9-10-46

[illegible]

(malononitrile) yield 75% (-10°, for [illegible])



A.H.

[illegible] (1946)

Vol. 18, p. 723-751

[illegible]

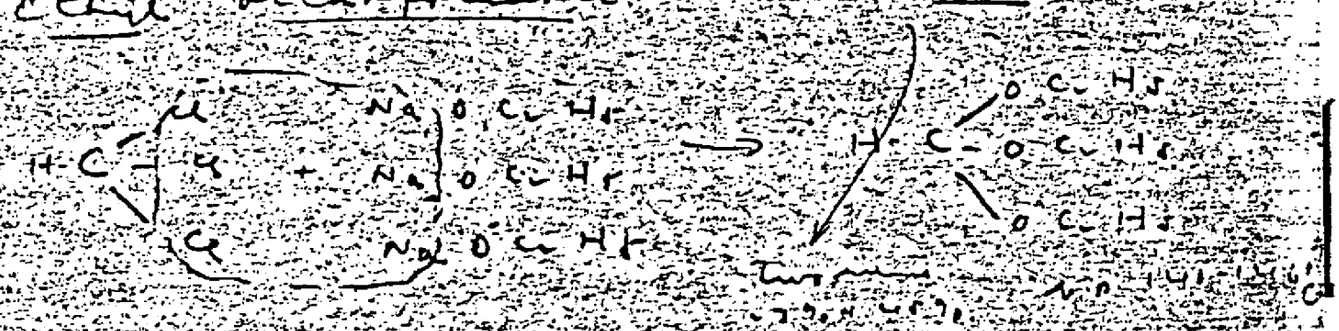
[illegible] p. 723-727

Org. Syn. Coll. Vol. II, p. 379-381 [illegible]

Org. Syn. Coll. Vol. II, p. 379-380 [illegible]

Cyanoacetamide [illegible] yield 87%

Ethyl orthoformate yield 73% (Arch)



Org Syn Coll Vol I p 258-261

W.E. Kaufman + E.E. Dreger

B1

CA 39, 1021 (1945)

Vitamin B1 is obtained by condensation of 2-methyl-4-amino-5-bromopyrimidine with 4-methyl-5-(β-hydroxyethyl)thiazole by heating in solvents of low dielectric constants such as benzene or xylene

U. Gm, Magdeburg C. A. I. Farben Nov 59,217 Jan 30, 1941.

CA 39, 3859 (1945)

Synthesis of Vitamin B1. N. Sugiura J. Pharm. Soc. Japan 62, 189-91 (1942). — The author prepared all modified as follows: mix an equimol. mixt. of 3.79 g. of 2-methyl-4-amino-5-(aminomethyl)pyrimidine with 5.2 g. of 2-methyl-2-(β-chloro-β-acetylpropyl)-3-thiazolotetrahydrofuran (4-chloro-4-acetyl-1-butyl-2-methylthiazolidine) (CA 39, 627D) add 79 g. H_2O and dil. to 25 cc. at 45-50°. Take up in 10 cc. 3N HCl in EtOH, add 3N HCl, evap. under reduced pressure to a small vol., and wash with abs. EtOH. Recrystallize 9 g. of dried material, m. 245-248°. Obtained from EtOH, mother liquor after crystallization from EtOH, [illegible]

A1

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

C1

[illegible] 1205

[illegible]

CA 39, 4486 (1945)

Imperial Chemical Industries, Ltd. from Nicholas Coates & Edmund G. Hunter Nicholls, Aaron Cohen, & Edmund G. Hunter

British 559,106, Feb. 3, 1944

Prepared by condensing 2-methyl-4-amino-5-thiformyl-aminomethylpyrimidine with the crude product obtained by the action of the dichloride or dibromide of methyl acid salts of tertiary N-alkyl-substituted thiazolines such as propyl-N-methyl-4-methyl-5-methylthiazoline.

Nothing of Value

D2

(4) (a)

CA. 38, 5855 (1944)

Preparation of edible mucilage. A. Brown. Pacific Drug Prod. 1, no. 3, 30 (1941). — Solution is synthesized by the hydrolysis of a 60% solution of gum in water with a Na catalyst at 60-70° then in water with EtOH, purified and 120° after cooling with EtOH, purified and neutralized to pH 7.0-7.2 yield, and concentrated and refined, final product can be used as a suspending agent for gelatine or as a suspending agent for gelatine particles. It is also used as an intermediate in the manufacture of acetic acid.

9-17-43

B1 1944

1289

B2

P1772

P2271

C

1739

CA 34, 1279[illegible]

a technological process for the production of ascorbic acid (vitamin C). 8.0 considerable [illegible] Truhlar Usenovich, Kuperman Esir, Vitamins (Moscow, Pub. 1940, 1939); 1941, 154-6; Khim. Referat. Zhur. 4, no. 29, 71-2 (1941).

Sorbitol is oxidized in 96-98% yield by hydrogenating glucose at 80 atm and 100-200°C for 40-60 min. The sorbitol is oxidized to sorbose by acetobacter at 28-30°C (yield 60%; m. 162-5°C). Sorbose is condensed with acetone in the presence of $CuSO_4$ and H_2SO_4 to [illegible] and diacetonesorbose. Diacetonesorbose is oxidized by [illegible] quate in alk. soln. to diacetone-2-keto-gulonic acid. This is split from the gulonic acid by $CHCl_3$ and saponified [illegible] for 40-50 hr in the presence of alc. HCl. The yield of ascorbic acid is 15-17% (based on sorbose). For industrial scale production the method must be improved to increase the yield of to decrease the loss

(2) 9-10-46

C.A. 38, 1752 (1944)

Isoallocaine derivatives. Roche Products, Ltd., Frank Hull, Aaron Cohen, and Frank Wynne. Brit. 550,836, Jan. 27, 1943. The synthesis of isoalloxazine derivs. 2:9 substituted (vitamin B_2) is carried out by treating 2-(α-nitrylamino)-4,5-dimethylazo-benzene with reduction products of alloxan, 2:9, alloxantin or dialuric acid. The azo compd. used as the starting material is prepd. by the method described by Kuhn.

also

C.A. 38, 1754 (1944)

Isoalloxazine. 1-N-Tetraacetyl-α-nitrylamino-2-hydroxy-4,5-dimethylbenzene to the Pfizer. R. Pattison & E. V. Brown. U.S. 2,332,666

Organic Synthesis ~~Texts~~ 0.50

Vol. 20 p. 74-76

(H.T. Clarke & S.M. Nagy)

Vol. 20 p. 14 to 16 (1940)

Synthesis 6.61

Anthraquinone Org. Syn. 20 p. 6-10

6/6/50

Cold NaOH

$H_3C-C\equiv N + HOC_2H_5 + HCl \longrightarrow H_3C-C(=NH)-OC_2H_5 \cdot HCl$

acetonitrile — acetimido ethyl ester hydrochloride

sp. gr. 0.783

b.p. 82°C

M.W. 41.0 — M.W. 123.5

Mix 41 gms. of acetonitrile and 46 gms. of EtOH

add 37 cc of ether (= 27 gms)

Cool to 0°C

Pass in HCl gas at 0°C

Let stand, beautiful shiny crystals are obtained

Filter off the crystals

Wash twice with 40 cc portions of Et_2O

Dry the crystals over H_2SO_4 in a vacuum desiccator

Transfer the crystals to a KOH desiccator and dry again in a vacuum to get rid of the last traces of excess HCl

Source: Berichte, Vol 16, p 1654 (1917)

(A Pinner)

C. 1948 (illegible)

CA. 37, 6096 (1943)

U.S. 2,378,[illegible]

M. G. Hall [illegible] application [illegible]

Einige Amidine der Chemie

N. Bull. Soc. Chim.

Vol. [illegible], p. 6[illegible] (1917)

[illegible]

[illegible] (1 mol) [illegible] (1 mol)

of [illegible] (1 mol)

[illegible]

[illegible] (1 mol)

If [illegible] add the two [illegible] heat

[illegible] [illegible] [illegible] reaction

[illegible]

The [illegible] [illegible]

[illegible] at 0°C, [illegible]

to bottom

After [illegible] (the deposition)

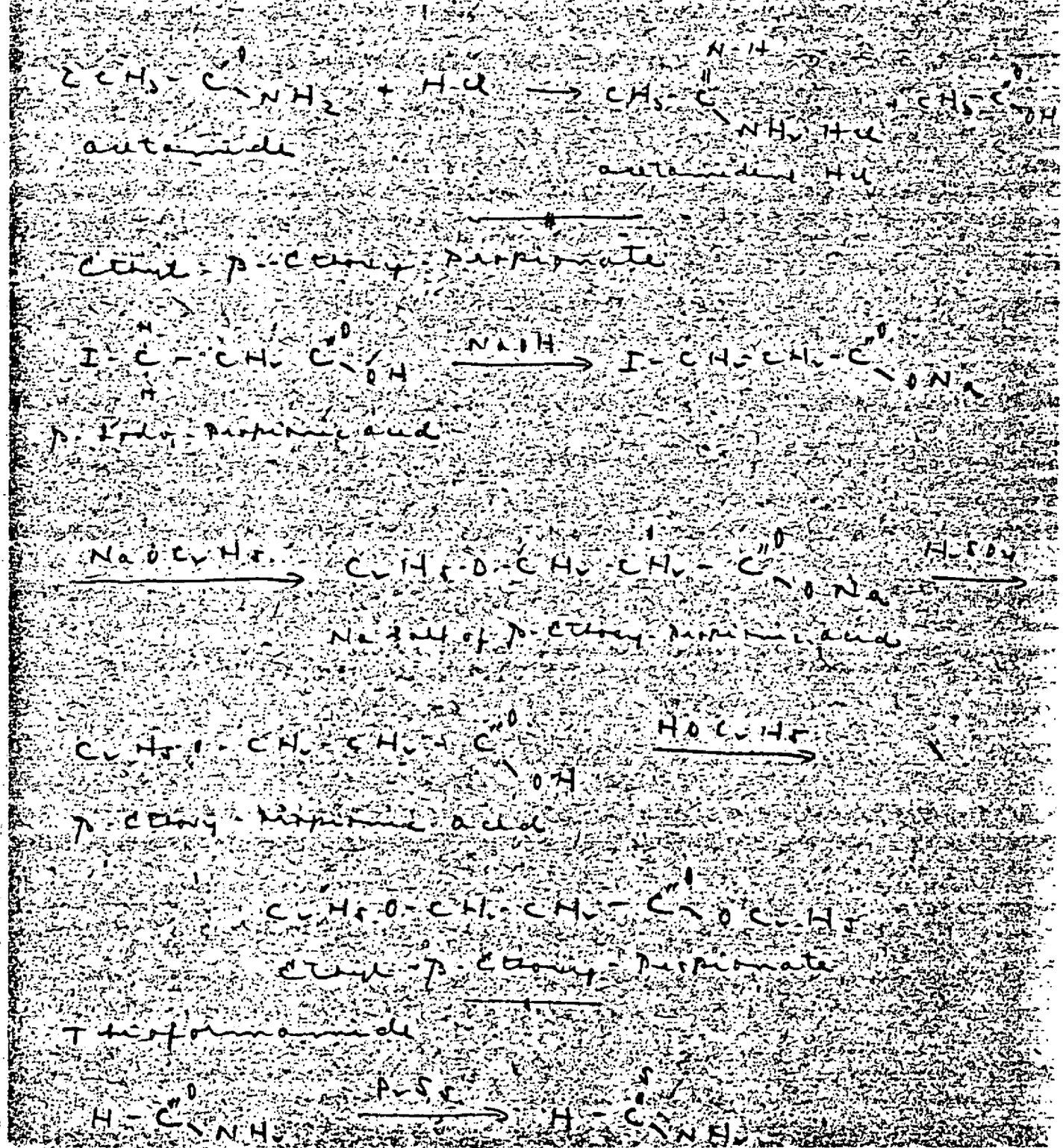
was [illegible] [illegible] Et₂O

[illegible]

[illegible] 6.0 [illegible]

Also, we propose to manufacture the following initial compds. for the synthesis

1. Acetamidine Hydrochloride



possible modifications in Vitamin synthesis

(Thiamin)

steps T.3 and T.4

α-chloro-α-acetoxy-butyrolactone $\xrightarrow[HCl]{H_2O}$

β-chloro-β-acetyl-propyl alcohol

and,

β-chloro-β-acetyl-propyl alcohol $\xrightarrow{\text{Thioformamide}}$

4-Methyl-5-β-Hydroxy-Ethyl-Thiazole

may be condensed to one step,

α-chloro-α-acetoxy-butyrolactone $\xrightarrow{\text{Thioformamide}}$

4-Methyl-5-β-Hydroxy-Ethyl-Thiazole

steps P.4, 5, and 6.

2-Methyl-5-Ethoxy-Methyl-6-amino-Pyrimidine $\xrightarrow[HBr, AcOH]{HBr}$

2-Methyl-5-Bromomethyl-6-amino-Pyrimidine Hydrobromide

and,

2-Methyl-5-Bromomethyl-6-amino-Pyrimidine Hydrobromide

$\xrightarrow{\text{4-Methyl-5-β-Hydroxy-Ethyl-Thiazole}}$

Vitamin B1-Bromide-Hydrobromide

or

Vitamin B1-Bromide-Hydrobromide $\xrightarrow{AgCl}$

Vitamin B1-Chloride-Hydrochloride

(2)

2-Methyl-5-Cyano methyl-6-amino-Pyrimidine $\xrightarrow{HCl}$

2-Methyl-5-Cyano methyl-6-amino-Pyrimidine Hydrochloride

also,

4-Methyl-5-β-Hydroxy-Ethyl-Thiazole $\xrightarrow{HCl}$

4-Methyl-5-β-Hydroxy-Ethyl-Thiazole-Hydrochloride

so that,

2-Methyl-5-Cyano-methyl-6-amino-Pyrimidine-Hydrochloride

4-Methyl-5-β-Hydroxy-Ethyl-Thiazole-Hydrochloride

Vitamin B_1-Chloride-Hydrochloride

P2 (Rubroplasmin)

None

Scheme C (continued)

steps 4 and 5

Diacetone-l-sorbose $\xrightarrow[KOH]{KMnO_4}$

monoacetone-l-sorbose $\xrightarrow[H^+]{H_2O}$ 2-Keto-l-gulonic acid

and,

2-Keto-l-gulonic acid $\xrightarrow{CO_2 + H_2O}$ l-ascorbic acid

may be condensed to

Diacetone-l-sorbose $\xrightarrow{H^+}$ l-ascorbic acid

CA. 29, 3978[5]

A new way of using CaC_2

L. Karjarian

J. Gen. Chem. (U.S.S.R.) 4, p. 1347 to 1352 (1934).

To obtain 3-methyl-3-hydroxy-1-butine (I), 150 gms. of dry Et_2O was mixed with powd. KOH (56 gms.) and 100 gms. of CaC_2 (equiv. to 1 mol. of C_2H_2). Acetone was added dropwise, (58 gms. in 1.5 hrs.), with cooling and stirring. The mixt. was stirred for 2 hrs. more, and the flask left in ice water till the following day, when 150 gms. of water was slowly added. The Et_2O layer contained I, b.p. 98-99° (yield 70%, referred to acetone).

To prep. 2,5-dimethyl-2,5-dihydroxy-3-hexine (II), 56 gms. of KOH and 100 gms. of CaC_2 were suspended in 100 cc. of Et_2O and 58 gms. of acetone were added during 1 hr., the reaction mixt. being kept at 6-7°C. Et_2O (70 cc) was added next to facilitate stirring. After 3 hrs. more, the mixture solidified. It was decomposed on the following day at 7°C with 150 cc. of H_2O. The Et_2O layer contained II, yield 74%, and 1 gm.

(2)

A New Way of using CaC_2

mixt. was added to an excess of acetone, the yields of I and II equalled 61.4 and 34.5% resp. K. suggests that CaC_2 and KOH form $K \cdot C \equiv C \cdot CaOH$ which combines with either one or two moles of acetone. In the first case, subsequent action of H_2O produces I; in the second case, II.

C.A. 33, 1269[9]

A. T. Babayan disputes K's mechanism and says CaC_2 acts directly

J. Gen. Chem. (U.S.S.R.) 8, 602-6 (607 in Fr.)

C.A. 32, 7894[3]

II - b.p. 206°C

2,150,523

2,150,948, (947)

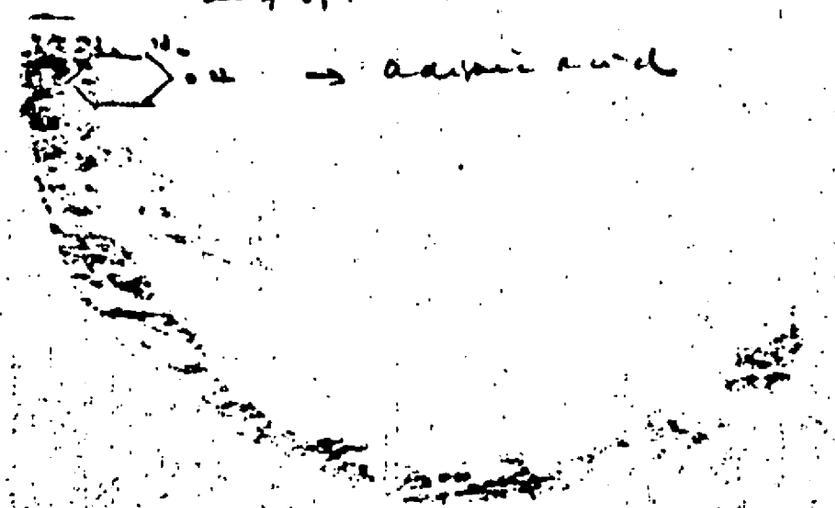
2,158,064

2,163,584 [illegible] S.R. [illegible] [illegible] [illegible] [illegible]

2,165,053 Dermitz of Reactor Aq etc S.W. [illegible]

2,361,717

1,941,101 Walter H Schmitt aug 8, 1933



→ acetic acid

31, 655

32, 0K.

33, 993 [illegible] 490,[illegible] aug 16, 1938 [illegible]

33, 559 [illegible] 490,636 [illegible] 1, 1938

34, 6307 U.S. 2,200,734 may 14, 1940 H.R. Arnold & W.A. Langley

2 screws holding metal reflector to prism box of Abbe' refractometer

Serial No. Wayne

U09863

1 Universal take-off stuffing head

1 Lab. Grinder, "Nurse Type" capable of delivering a 5-P7, Gore-Tex [illegible]

1 ~~Dome~~ for 7½ x 14 with Dermator Type Flange & equipped with a [illegible] Head providing for

a- agitation

b- a [illegible] tube

c- a take-off tube

[illegible]

Gen. Formula – $C_nH_{2n}O_2$

Nomenclature

1. Acetic

$CH_3-CH(CH_3)-C(=O)-OH$ 3-methylbutanoic acid

2. Carboxylic acids

$CH_3-CH(CH_3)-C(=O)-OH$

2-methyl-1-propanecarboxylic acid

3. Acetic acid derivatives

$CH_3-CH(CH_3)-C(=O)-OH$ isopropylacetic acid

Name formula

acetic CH_3-COOH

propionic CH_3-CH_2-COOH

butyric $CH_3-CH_2-CH_2-COOH$

valeric $CH_3-(CH_2)_3-COOH$

caproic $CH_3-(CH_2)_4-COOH$

caprylic $CH_3-(CH_2)_6-COOH$

lauric 12

myristic 14

palmitic 16

stearic 18

Conference 3-11-47

1. Monomer Synthesis
2. Powder Polymerization
   a. Compression molding Type
   b. injection " "
      extrusion " "
3. Sheet or Bulk Polymerization

Monomer Synthesis

110 gm KOH
230 gm. methylal
37 gm acetone

1. Ni catalyst for C_2H_2 addition.

	Mol wt	Theo wt	yield, gm.
110 gm KOH	1.96	0.64	37.7
230 gm. Methylal			
37 gm. acetone	0.64		

(110) - [37]

$$2\,KOH + H-C\equiv C-H \longrightarrow KC\equiv C-K + 2\,HOH$$

$$\xrightarrow{2\,MeCO} H_3C-\underset{\underset{\underset{\underset{OK}{|}}{C}}{|}}{\overset{\overset{K}{|}}{C}}-CH_3$$

H_2O Produced

$$\frac{18}{58} \cdot 37 = 23.6 \text{ gm. } H_2O$$

$$\begin{array}{r} 4 + 74.3 \\ \hline 97.9 \text{ gm. } H_2O \end{array}$$

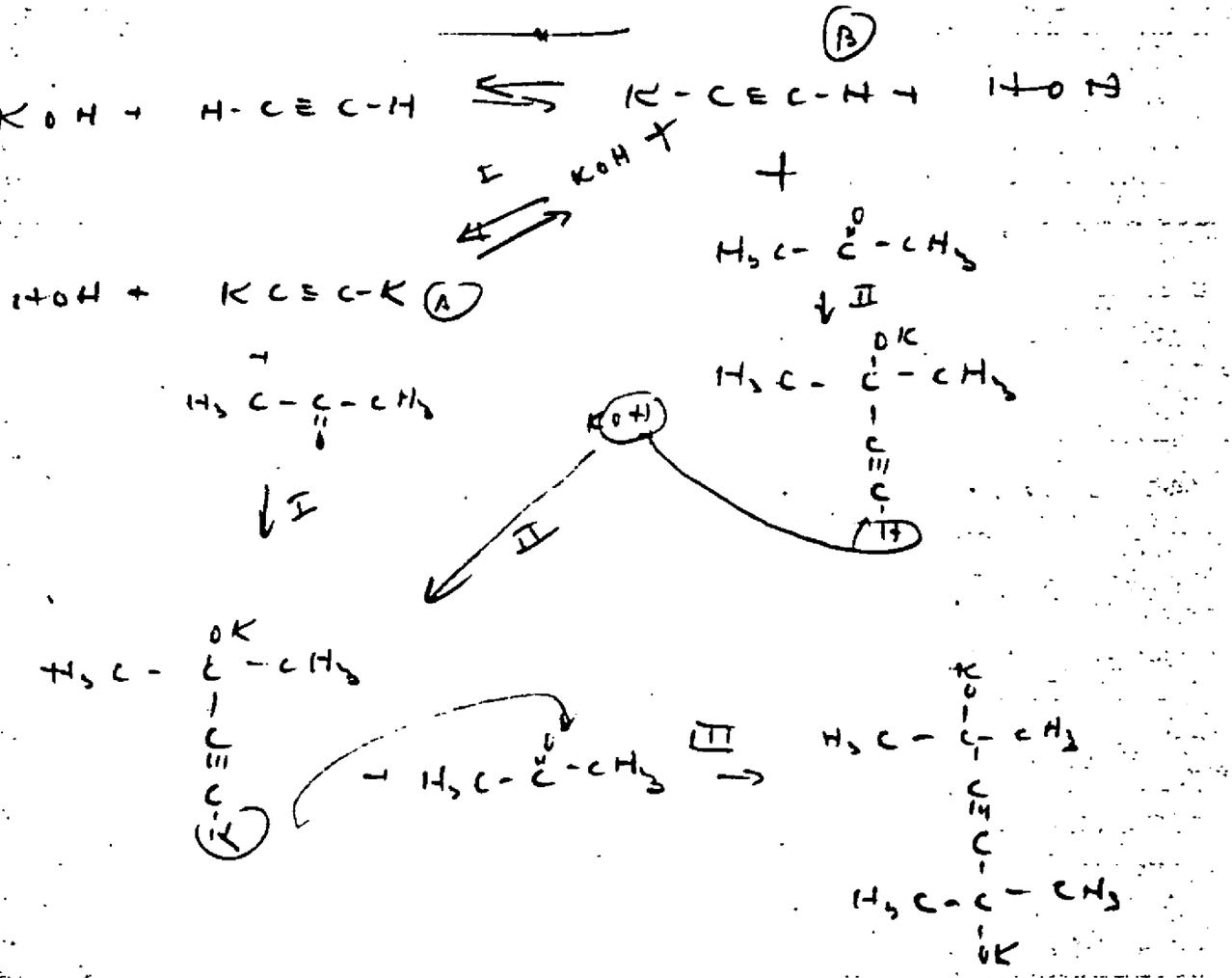
$$\frac{74.3}{97.9} \cdot 37 = 28.1 \text{ gm. [illegible]}$$

(2) 3-11-47

Can produce

$\frac{142}{116} \times 37 = 45.3$ grams. Need (& need 110 grams KOH for this)

∴ must continue process from standpoint of C_4H_6 adder.

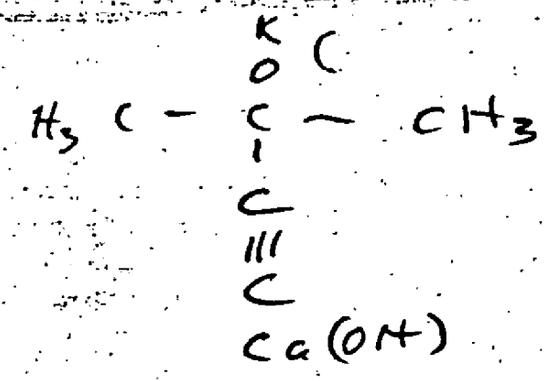


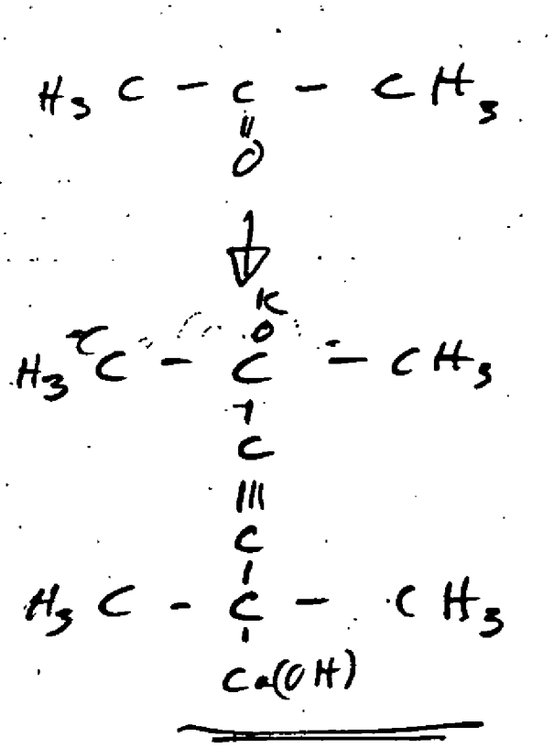
Therefore arrive at K salt of Butinol by two methods I & II.

So if we have (A) & (B) present in excess we can only get Butinol.

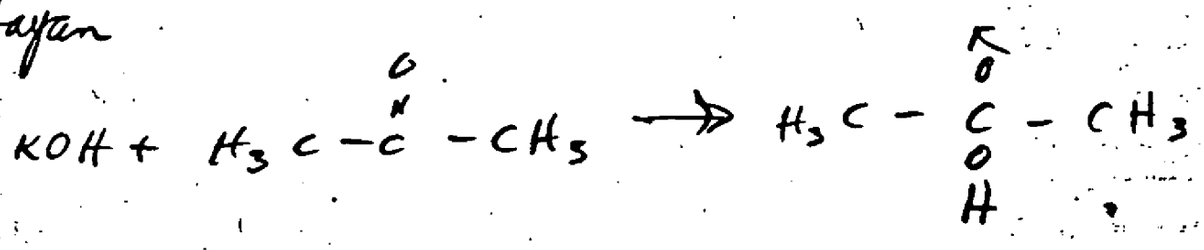
Why raise t° to 13°C for MgEtCl adder?

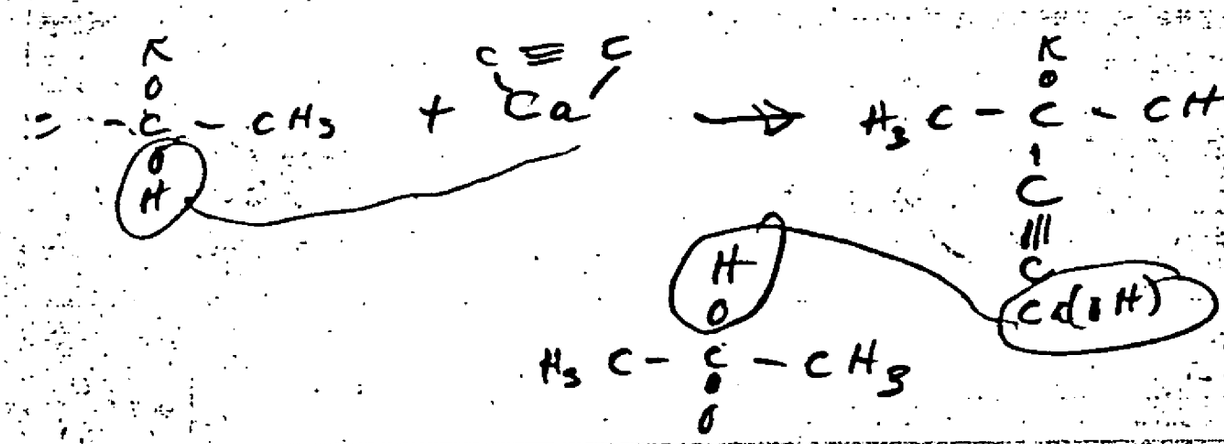
Ans. Because we have exothermic reaction (like

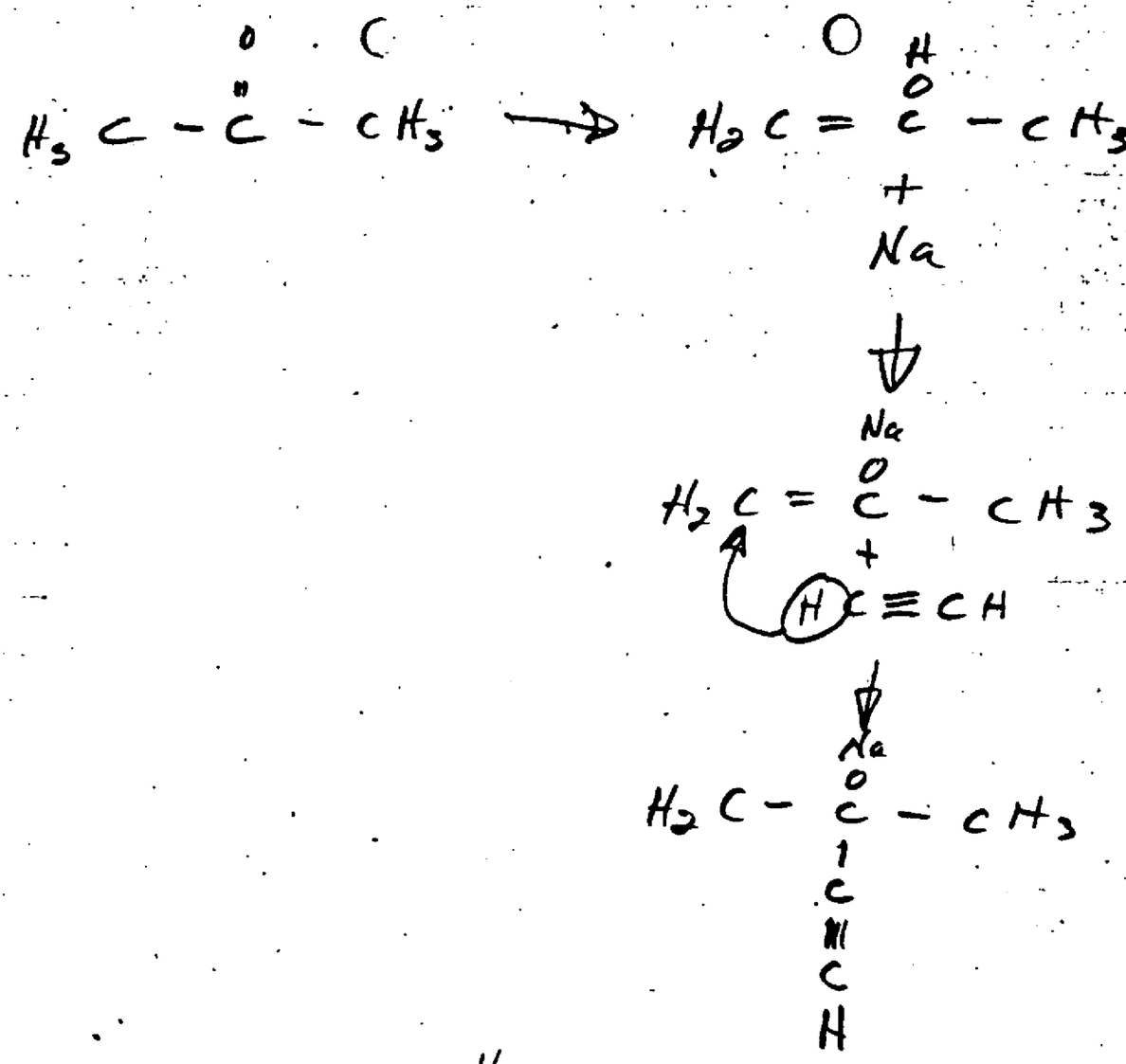




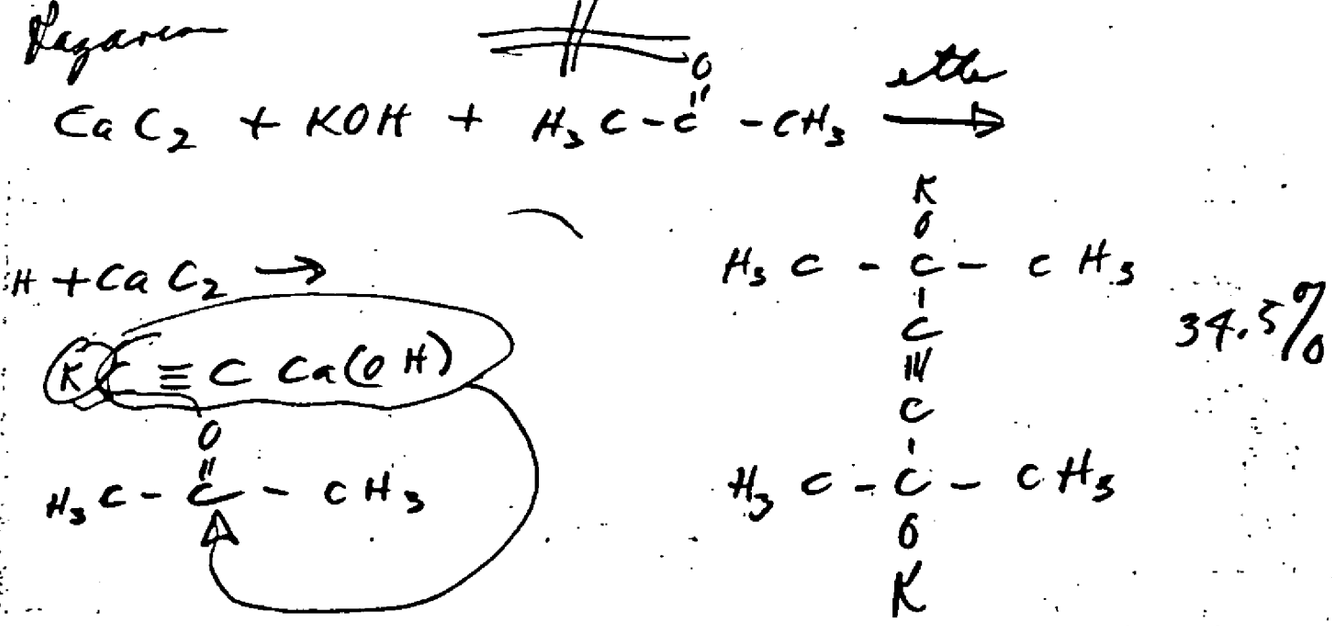
Jawaban

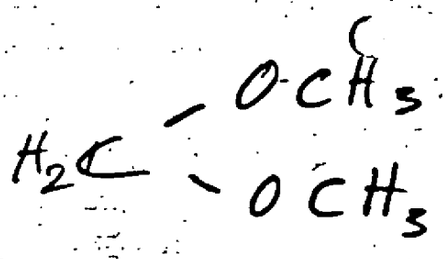


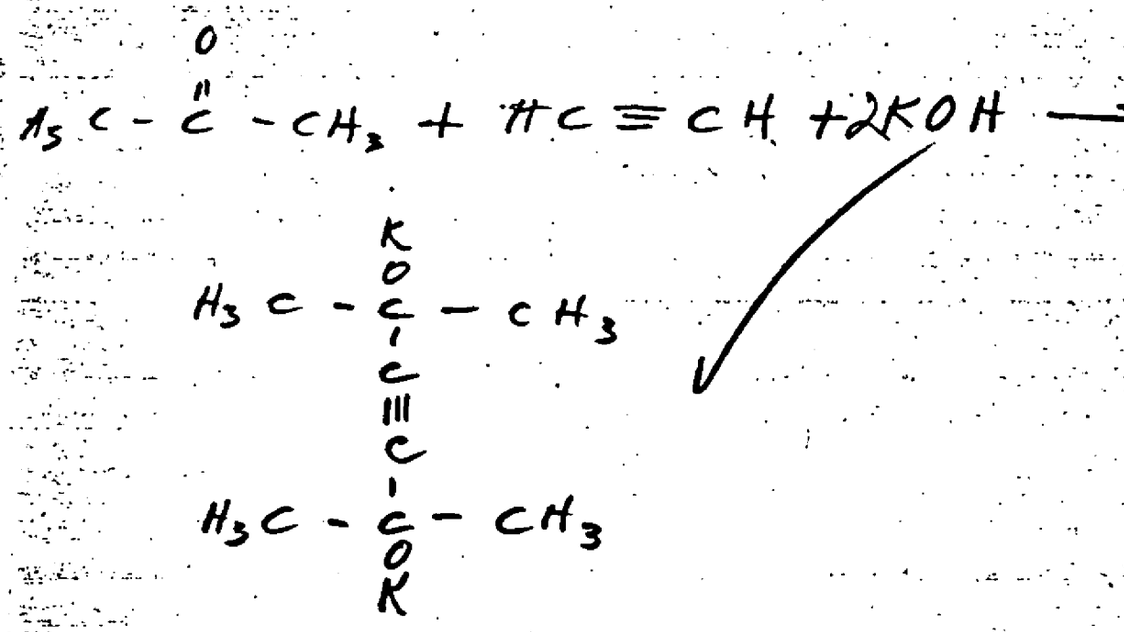


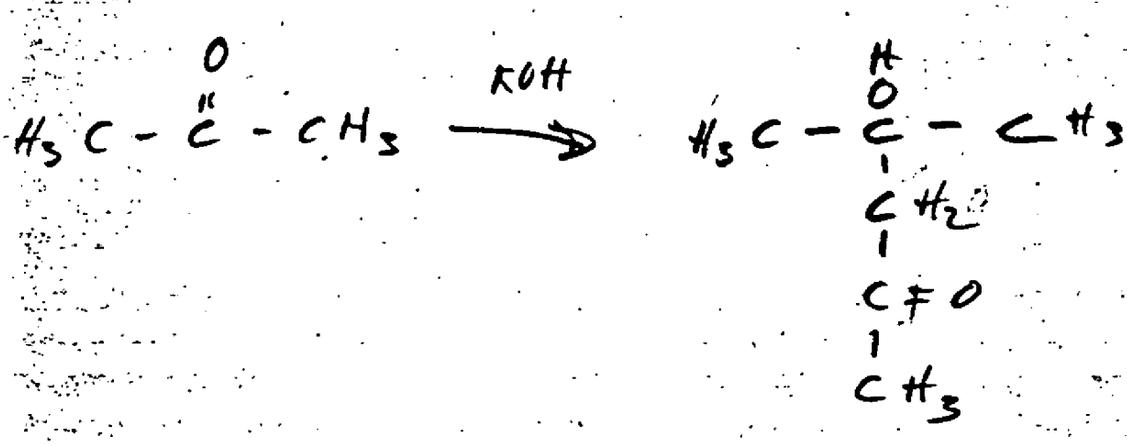


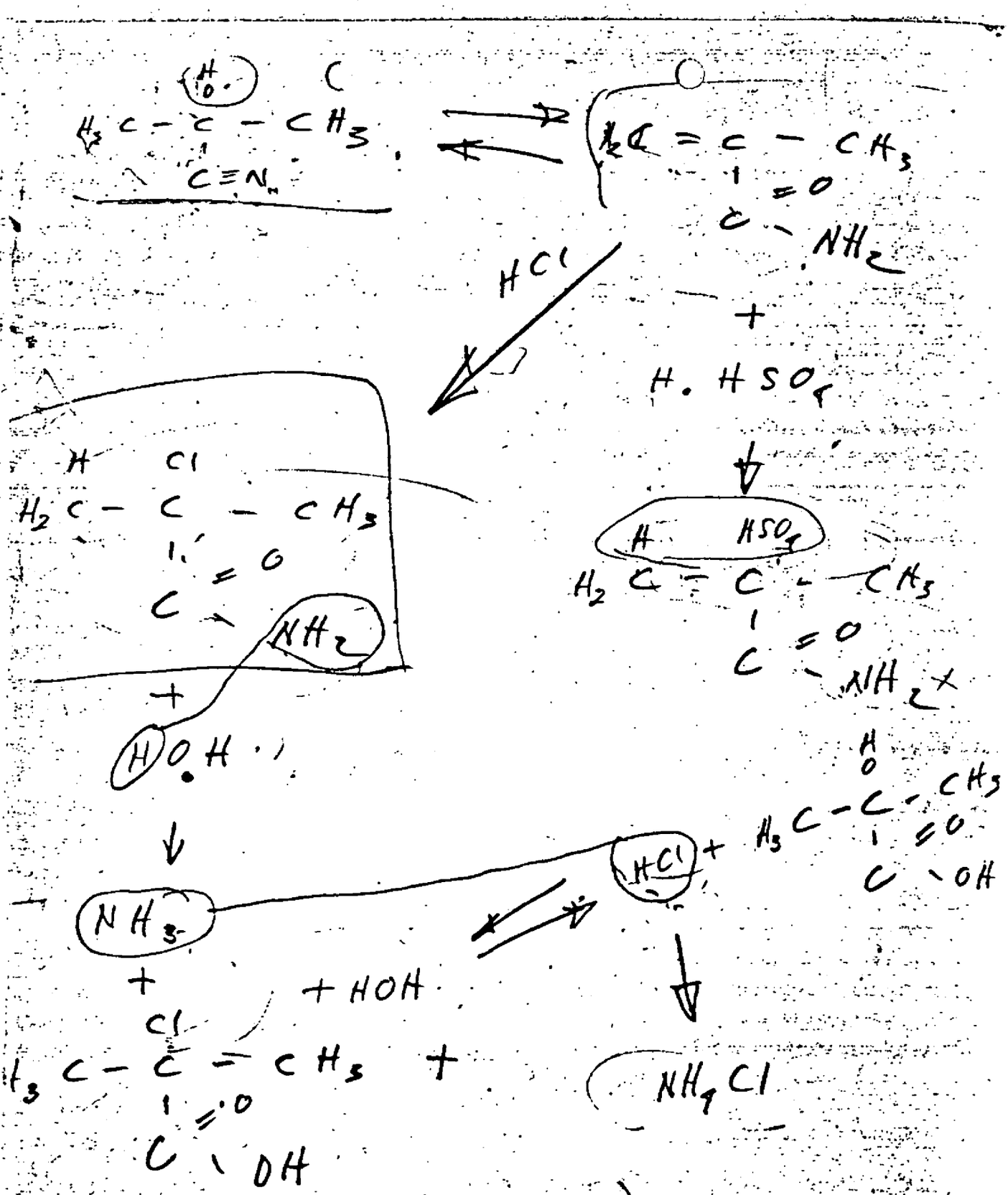
Pagario



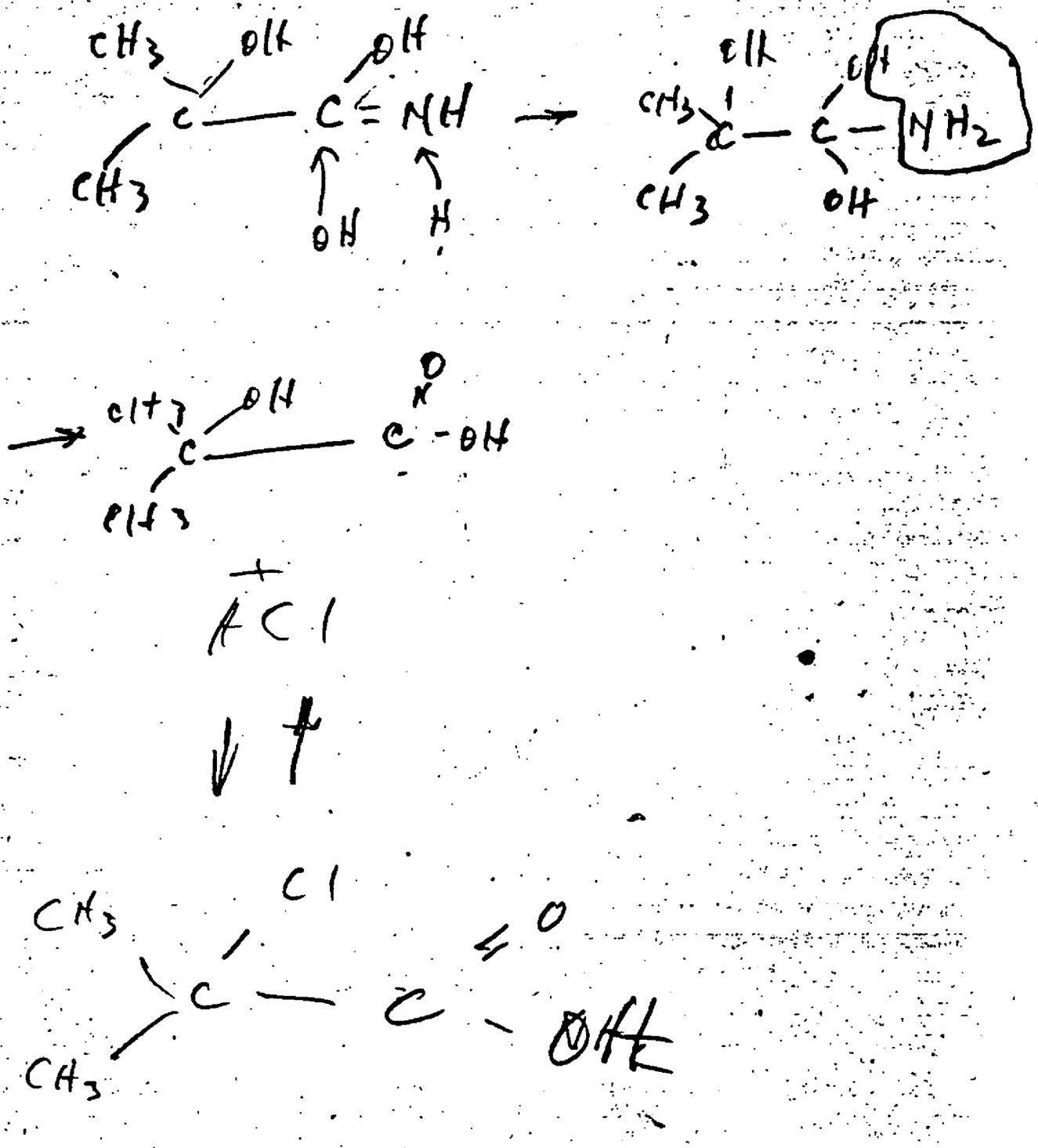







HCl
H. HSO4
NH3
+ HOH
NH4Cl

C O


CH3
OH
OH
C
C = NH
CH3
OH
H
OH
CH3
C
C
NH2
CH3
OH
CH3
OH
O
HCl
CH3
C
Cl
O
C
OH
CH3

6/6/50

2.7691

Opt. ① 22.8011
19.2360
3.4751
.5838
4.0589 m

② 19.8076
19.3238
.5838 mp

$\frac{4.0589}{238} = \frac{x}{58}$

$x = 0.989$ g

~~Water layer~~
~~12.4156~~
~~8.1583~~

% $= \frac{98.9}{2.77} = 35.7\%$

Sample ~~B~~ ③ 10.1587
8.1592
1.9995

Op. 21.0362
16.7860
4.250

$\frac{4.25}{238} = \frac{x}{58}$

$x = 1.0357$ g of "acetone"

% $\frac{1.0357}{2.0} \times 100 = 51.8\%$ mp 163°C

$KOH + HC{:}CH \rightleftharpoons HC \equiv C^{-} + H_3C-\underset{\underset{O}{\|}}{C}-CH_3$

$aC_2 + KOH \rightarrow$

$KC \equiv C\ Ca(OH)$
$+$
KOH

$\downarrow$

$\boxed{KC \equiv CK} + Ca(OH)_2$

$H_3C-\underset{\underset{O}{\|}}{C}-CH_3$

$\downarrow$

$H_3C-\overset{K}{\overset{O}{C}}-CH_3$
$|$
C
$\equiv$
C

$K + KOH \rightarrow HOH +$

$\downarrow$

$CH_3-\overset{OH}{\underset{CH_3}{C}}-COOH$

$C_4H_8O_3$

$H_3C-\underset{\underset{O}{\|}}{C}-CH_3 \rightleftharpoons H_2C=\underset{\underset{O}{|}}{C}-CH_3$

$H + KOH \rightarrow$

$\frac{5.4}{16}$ keto

$\frac{0.0023}{81.4} = 0.000283$ mols

$\frac{575}{183} = \frac{8\,6\,L}{8\,5\,L}$ 0.085 1.861

$\frac{0.001}{18} = \text{mols } H_2O = 0.000555$

$0.0085 = 169.4x + \%_{H_2O}$

$H_3C-\underset{\underset{O}{\|}}{C}-CH_3$

$HC \equiv CH$

OCH_3
H_2C
OCH_3

$m = 65.4$
$C_4 = 48.$
$H_8 = 8.$
$O_3 = 48$
169.4

$\frac{2\sqrt{2}}{1\sqrt{5}}$
$\frac{1\sqrt{5}}{37.\sqrt{5}}$
169.4

Solvent for KOH (ethyl + water)

$2KOH + CaC_2 \longrightarrow K_2C_2 + Ca(OH)_2$

$+$

$HOH \longrightarrow$ Sand

$\downarrow\uparrow$

$CaO + HOH \rightleftarrows Ca(OH)_2$

$+$

C_2H_2

$+$

$KHC_2 \longrightarrow$

$+$

KOH

Intro greater dehydrating potential

1. Fusion ✓ & ✓
2. Must dehydrate KOH
3. $Ca(OH)_2$ formation → ppt.
4. Temp. dependent control (may be diff. for diff. colleges).

1. Prior art
2. Statement (not necessarily accurate)
3. Theory
4. What we claim

457 508

10 50

$$\ln \frac{508}{457} = K\left(\frac{1}{10} - \frac{1}{50}\right)$$

$$0.1052 = K\left(0.1 - 0.02\right) = 0.08\,K$$

$$K = 1.318$$

$$\ln \frac{457}{x} = 1.318\left(\frac{1}{2} - \frac{1}{10}\right) = 1.318\left(0.4\right) = 0.527$$

$$\frac{457}{x} = 1.695$$

$$x = 270$$

$$\ln \frac{457}{3.03} = 1.318\left(\frac{1}{x} - \frac{1}{10}\right)$$

$$.411 = 1.318\left(\quad\right)$$

$$\frac{1}{x} = .412$$

$$x = 2.43$$

$$1 \quad , = .317$$

$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$

A — 0 K + HOH

HOH $\rightarrow$ $\frac{1}{2}$ C_2H_2

$\boxed{\frac{1}{2} \text{ mole}}$

CaC_2

80 gms.

Fraction 4

Sample — 10.0000
8.1596
2.4764

200 ml of phenyl hydrazine

Wt. of ppt. 17.6000
16.8447
.7553

250

8.7364

Analysis of Acetone Solutions – Run 7

Fraction 1

		25.2513	26.1029
		23.1595	23.3232
		2.0918	2.7797
			2.0918
			4.8715
Ppt.	19.7715		
	19.7273		
	.442		

Fraction 2

		28.2842
		23.1607
		5.1235 g Sample
Ppt.	19.7107	
	19.2194	
	.4913	

Fraction 3

		25.7350
		23.1602
		2.5748
Ppt.	19.5867	
	19.2516	
	.3351	

6/6/50

Leaching of Disk with CCl_4

170
110.3
60.3 g of residue

100 g of CCl_4

66 × 3

C O

$\frac{315}{142} = 50$

40
35

70 calcium carbide

70 g
0.8

65
7

45.5

$\frac{5}{2} = 0.317$ mole

$\frac{45.5}{64} = 0.71$ mole.

315
180
135

$315 \times 0.71 = 223$ gm

$\frac{315}{180}$ $\frac{135}{315} \times 0.71$

6 6

13.1
1.3
24.4

14 ans.

1070 1014

150
56
271

150
50
150
50
150

6/6/50

EXP. HEXINE

KOH — 330 gms (50)

acetone — 101 "

methylal — 810 " (50-75 cc used)

acetylene — 6 bubbles/sec.

dry ice — estimate

water & ice — 600 gms. (150 gms. as ice)

EXP. α-HYDROXY ACID

hexine — 50 gms.

chloroform — 500 cc.

H_2O_2 — 5 cc

H_2SO_4 — 2.5 gms. 40°C

EXP. METHYL BUTINOL

hexine — 50 gms.

$Ca(OH)_2$ —

EXP. Me Me -

α-hydroxy acid — 300 gms

ethanol — 367 " (462 cc)

95 — 110 "

1 cc methanol used on transfer to distillation equipment

tolyl sulfonic acid — 8 gms

10 cc	pH	5.6
2 cc		5.6
.6		5.5
1.6		5.4
2.0		5.3
2.0		
3.0		[illegible]
3.0		

4:10	Started heating	
25	temp	47°C
30	"	56 Clearing up
34	"	71
38		84 Reflux begins
45		92
50		94
5:08	Stop reflux	

20 cc. NaOH pH [illegible]

20 " " pH 7.4

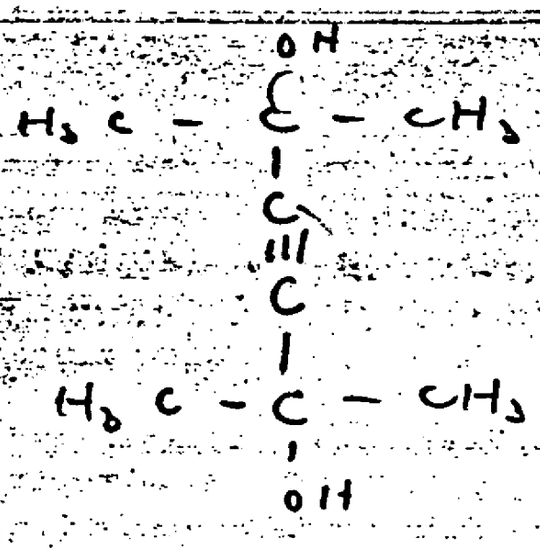
Started [illegible] station (methylal + KOH) at 11:00 am

Cooled to 0°C; started adding acetylene at 12:05

~~stopped~~ adding acetylene 12:25

Warmed up to 10°C

3:50 to



Ether Extractions

75 mls. X 2

25° " — III

~~Water added 75 mls.~~

633.6 — fuel

920 — flask

60
144

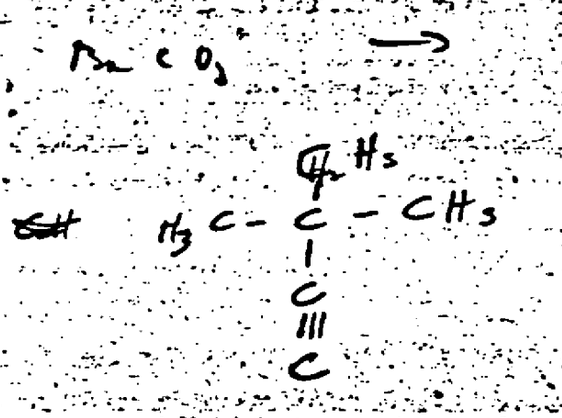
53
54
28

116
28
144

6/6/50

$BaCl_2 + NaOH \longrightarrow$

$BaCO_3 \longrightarrow$



Call Mr. Bronstein
Armory 4-6520

Powder CaCl
Wood filler (walnut shell)
Urea form mold powd. (or dry urea)
Urea

13-15 °C

Bring temp of reaction mix. to 0°C
add 50 g of crushed ice. not over 8°C
(try have at 0°C)
add 60 & 70 c.c. of water to dissolve

Pour in sep. funnel. Separate. Add 50-60 g
of dry ice

6/6/50

make set-up as (see Exp't C33 (with trap for methylal))

1. Place 425 cc of methylal in flask
2. Cool methylal to −10°C.
3. Pass in acetylene for 1 hr (no stirring)
   Place any trapped methylal back in flask.
4. Let the temp. rise (remove bath) to 15°C.
5. Cool quickly to −10°C.
6. Add 110 gms. of KOH, watch for heat rise, keeping the temp. at −10°C
   ↳ using agitation
7. add 45 gms. of CaC_2, keeping the temp at −10°C.
   ↳ using agitation
   Eliminate trap - see note below
8. Let temp rise to 15°C. agitate for 2 hrs to let K_2C_2 form.
9. Drop in (as rapidly as is consistent with keeping the temp. at 15°C) 43.5 gms of acetone. Try to have the stirring as efficient as possible during the acetone addition
10. Keep the stirrer going for 2½ hrs.
11. Decompose by the addition of
    a - 51 gms of ice + H_2O
    b - 62 gms of H_2O
12. Up top layer, neut. etc.

Note 9(a) at C_2H_2 [illegible] during 9 [illegible]

11-2-46

Time	Temp. Inside	Bath	Remarks
3:40	0 °C	- 8 °C	Temp. rose to +5°C
55	+2	- 7	45 drops/min.
			= 2.2 cc/min.
4:00	+2	- 9	
4:05	+4	- 10	Lowered rate to 5 drops/min
4:10	- 1	- 15	Lowered rate to [illegible]
4:20	- 2	- 15	
4:30	0	- 15	[illegible]
4:35	0	- 15	Additional [illegible] added
5:00	0	- 10	
5:20		- 5°	Sulfuric diluted
6:45			Reaction finished (over 4:00)

6:50 Distillation started

7:00 collected 1st fract. 20° - 40° C 22.8 gms.

7:10 collected 11.0 gms.

7:45

~~[illegible]~~ ~~[illegible]~~ ~~[illegible]~~ ~~[illegible]~~

32 16.8

~5 g. Monomer

75 mg

150 mg.

$$\frac{103}{58} = 1.78$$

$$2H_3C-\overset{\overset{O}{\|}}{C}=CH_2 + 2SCl_2 \longrightarrow 2H_3C-\overset{Cl}{C}=CH_2 + S + SO_2 + 2HCl$$

∴ 110 gm. acetone theo.

109.7

99.7 gm. acetone

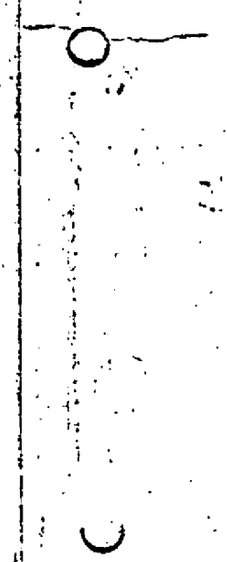
+ 2 CO2 + 2 H2O

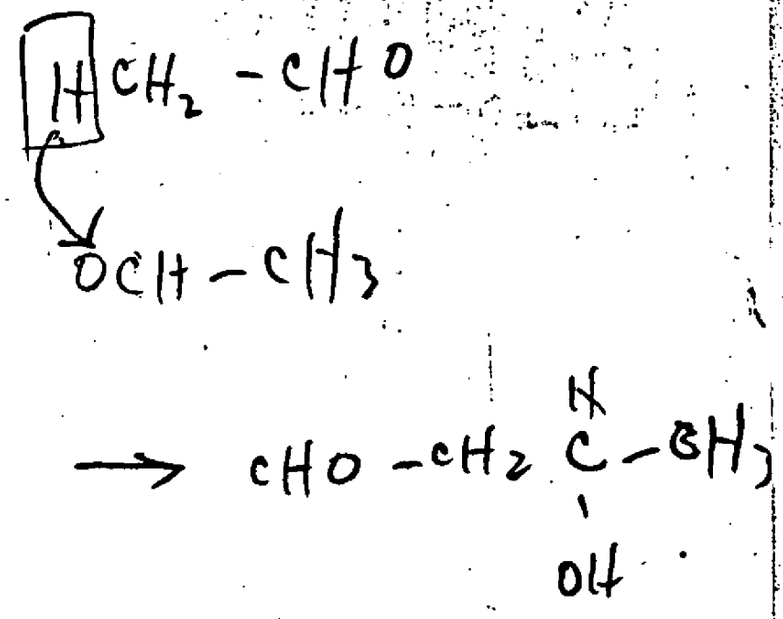
1-1-41

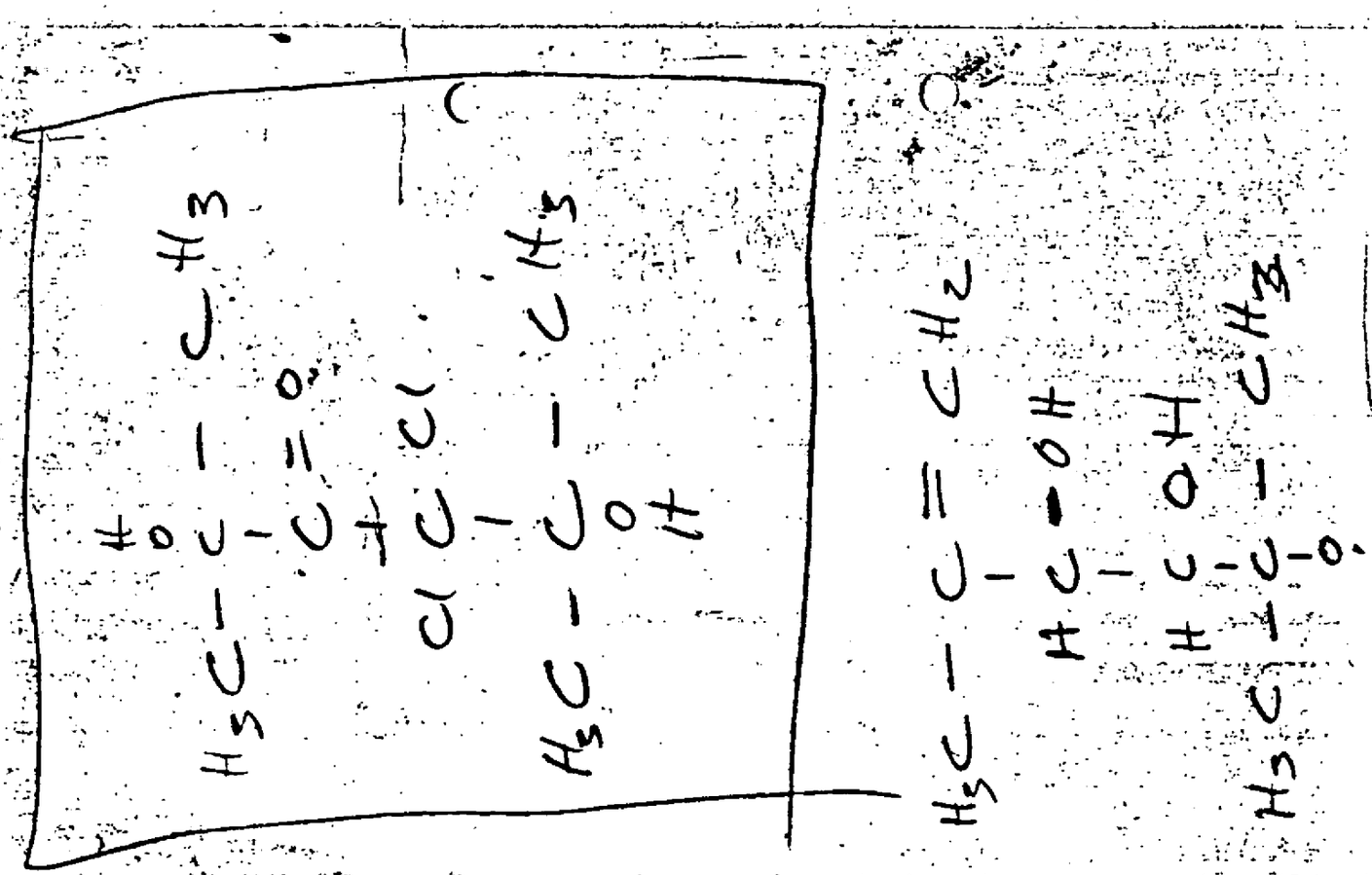
Experiment

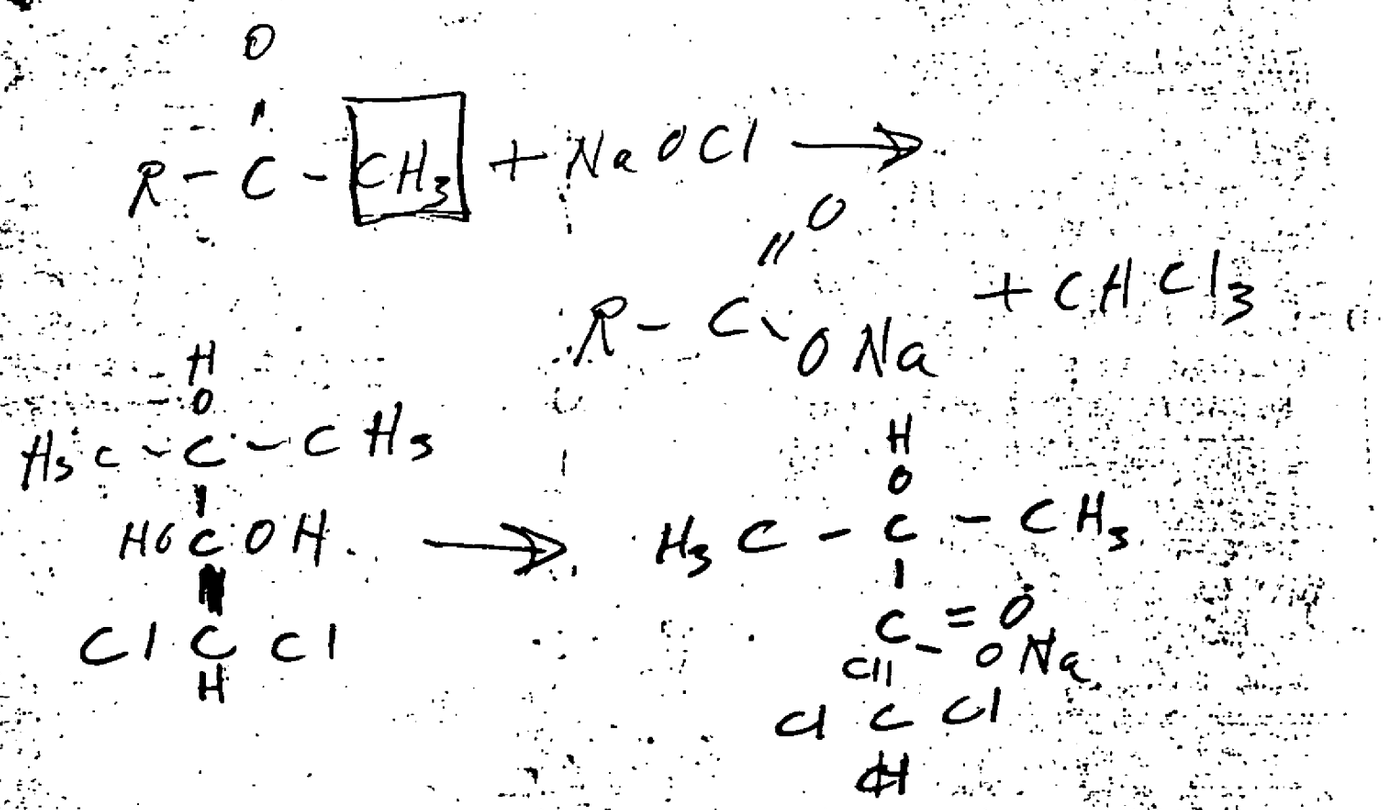
To 270 g of methylal added 110 g KOH while under stirring. Then added 45 g $CaCl_2$

Time	
3.50	Started adding C_2H_2
	Temp. kept at 13°C up to 4:30; after that bet. 14-15. Occasional warming required to keep the temp at 14-15°C.
5.50	Stopped adding C_2H_2
	Weight of material in trap 108.5 g. Returned this to the reaction flask.
6.10	Resumed adding C_2H_2 Started adding 49.5 g of acetone.
6.20	Finished adding acetone Temp. 13-15°C
6.30	Material in flask getting viscous. Occasional cooling required.
6.45	Stirring very poor.
7.00	Caked up; only very small hole around the stirrer.
7.30	Difficult to keep stirrer going.
7.50	74 g of methylal in the trap returned to the reaction flask; acetylene feed stopped.
9.10	50 mg of [illegible] added
9.20	50 [illegible] more added
9.30	13 cc of water




H
CH2 - CHO
OCH - CH3
CHO - CH2 C - CH3
H
OH





~~for 100% yield of product - every mol of CaC_2 must have reacted and for each mol of product, 2 mols H_2O are needed to hydrolyze~~

~~$\therefore 2 \times 4.5 \times 18 = 162$ gms. H_2O~~

$4.5 \times 300 = 1350$ mls. H_2O

3^{45} - start adding material to water - 5°

5^{25} - finished addition continual stirring to

6^{25} + place in refrigerator overnight.

Co 7 - 2119

after 1^{30} or before 12

11-21

① filtration on Büchner funnel with dry-ice acetone trap to vacuum line

② The product was a dark ruby red liquid the color of port wine

NO LAYERS -

③ no considerable extraction of color with ether, chloroform or acetone. ether + acetone miscible to a large extent with small test portions

④ *** on addition of HCl an oil separated out -

⑤ best method so far seems to be to add ether then water, + the color goes up to the ether layer - with addition of HCl to this, the upper ether layer loses some color to the ... to ...

100 mls. of product.

wash with 900 mls. H_2O
no separation

100 mls to 500 mls H_2O

) in test tube when small quantity was mixed with about 5x volume of water at first separation took place. On thru mixing, homogeneous - on addition of salt + shaking, an oil separated.

time	Bath T.	Reaction T.
1[17]	1P	2°
start adding		
2[00]	-1°	-7.5°
2[05]	-2	6.
2[13]	-2	6
light mud color of CaC_2 - KOH mix		
2[16]	0	6.75
2[24]	0.5	6.5
mud brown		
2[43]	-3	6
about 9/10 of dry mix added		
2[57] - all added		
	1	6.75
3[10]	3.5	7.5
3[53]	4	6

about 10 min. at 6-9°. then lowered

4.5 x 400

4.5 x 56

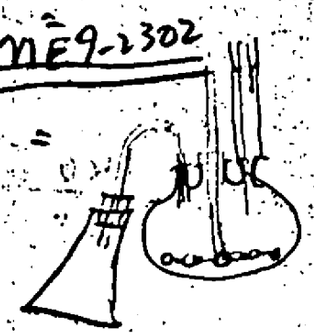
4.5 x 75.4 =

80 g.

May Urbank

Hawlick

NE9-2302



① 80-87% - (av. 84-85%)

② available - Keokuk, Iowa

24 x 2 lbs. cans -

$10. f.o.b. - powdered

carbide

adapters - A 1-110

1 2 200

amy acetone

amy. KOH

amy. CaC_2

39.
17
56

$\frac{56}{0.85} \times 4.5 = 296$

powder funnels

A 36-870

CaC_2

6.0

fac - 2.26

394

280
28
252

Quantities

CaC_2 — 360 gms. (80% CaC_2

Acetone — 1800 gms.

KOH — 296 gms. (85% KOH

$FeSO_4$ — 1 lb.

— H_2O_2 (30%) — 1/4 lb.

$CHCl_3$ (sieve)

---

65 g. CaCl

~~1200 g — 1500 cc~~

5 l

1000 g

~~1000 g~~ = 540 cc

5 x 56 = 280 gm KOH

5 x

30 16 12 56	8 4.5	400 9.5 2000 1600

65 g

CaC_2 → $HC \equiv C-H$

40

64 → (26)

acetylene

tot — 755

1800

2555

$\frac{64}{0.85}$

0.85

CaC_2	KOH
tot — 306 360 666	tot — 666.2 296.0 962.2

$\frac{64}{0.85}$ = 75.2 gms CaCl

$\frac{64}{0.80}$ = 80 gms

4.5

400

320

360

~~X 5~~

6/6/50

Mr. Dougherty

CO 7-2119

100 g. calc. = 1 Oxalic acid + H_2SO_4

40
-4

64 → 28

$\frac{100}{64} \times 28 = 43.6$ g.

= 64.3%

$H_3C-C(OH)-CH_3$

$HO-C-OH$

$Cl-C-Cl$
OH

Conclusion

$C(=O)-OH$
$C=O$

$C(=O)-OH$
$C=O$

$\frac{43.6}{100}$

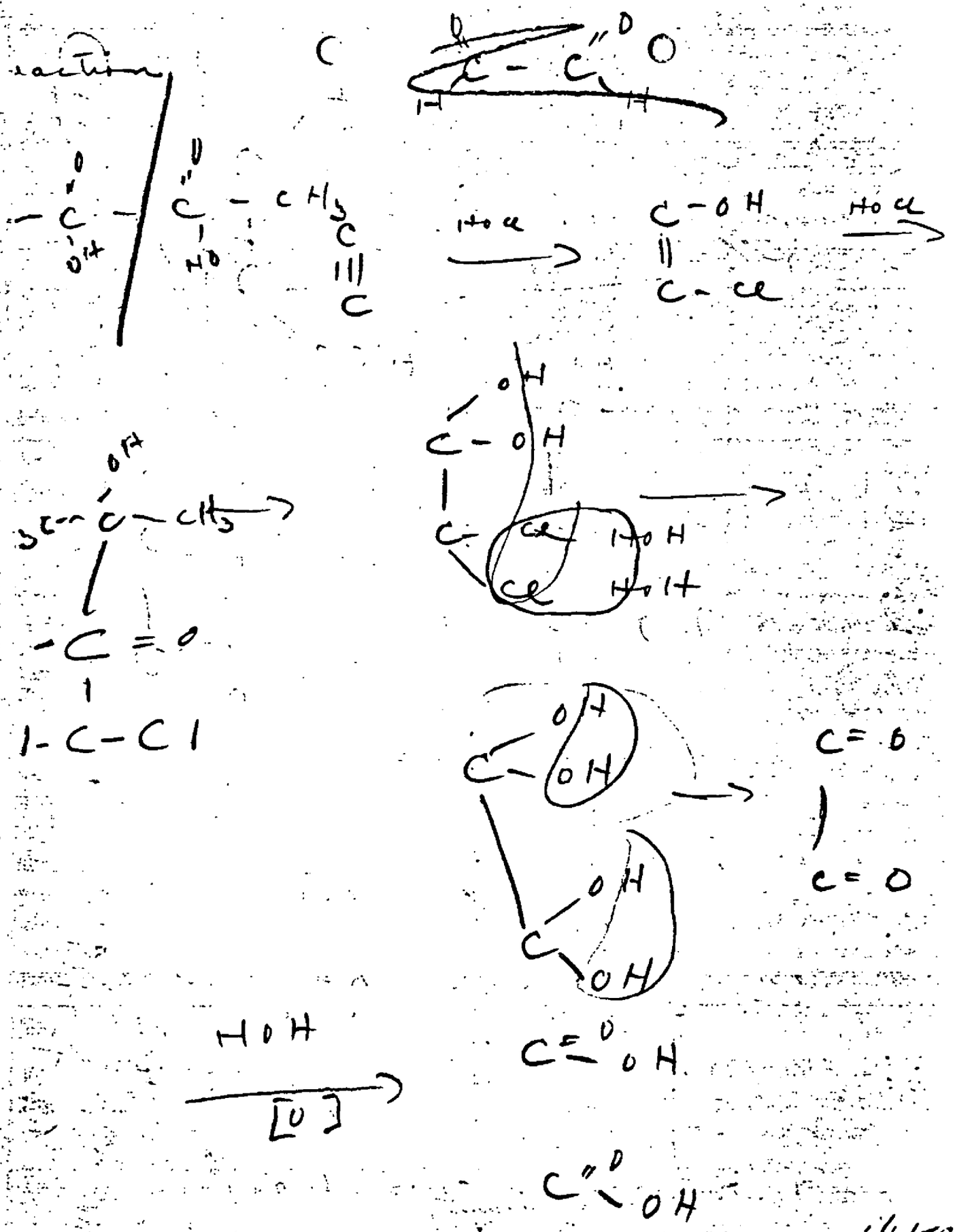
43.6

0.3

5 (20)

0.3

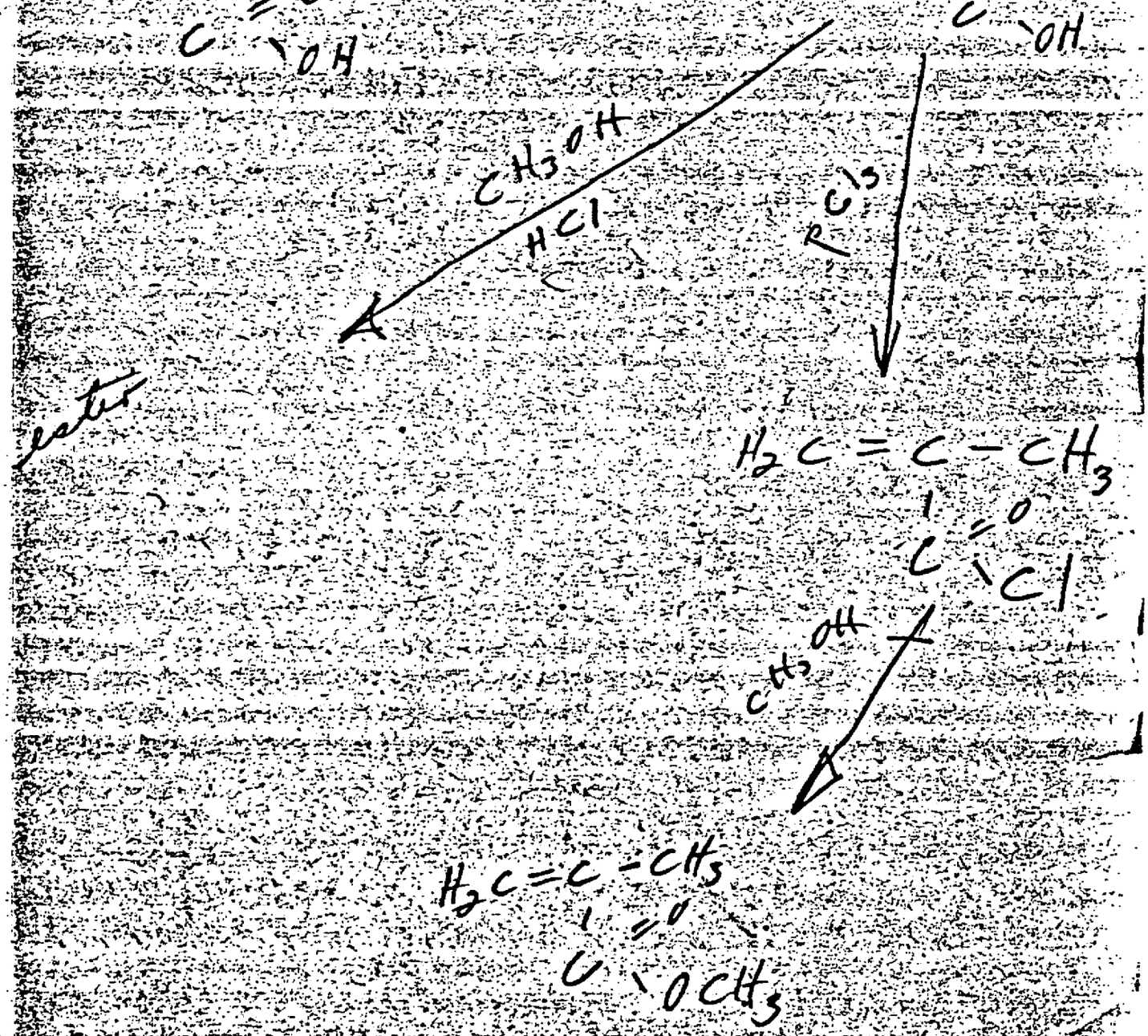
265



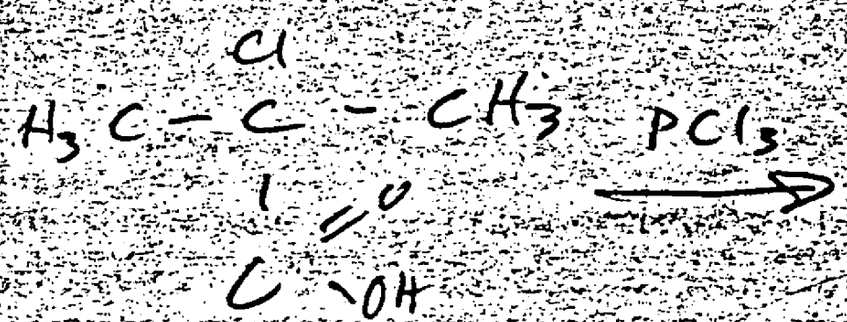
6/6/50

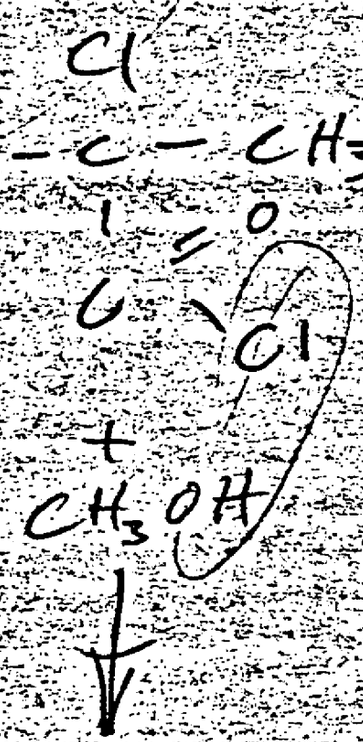
Class I (1)

1. removal of OH group from Resine & butine cpds.
2. oxidation of chlor substituted ~~isobutyric acid~~ Resine & butine



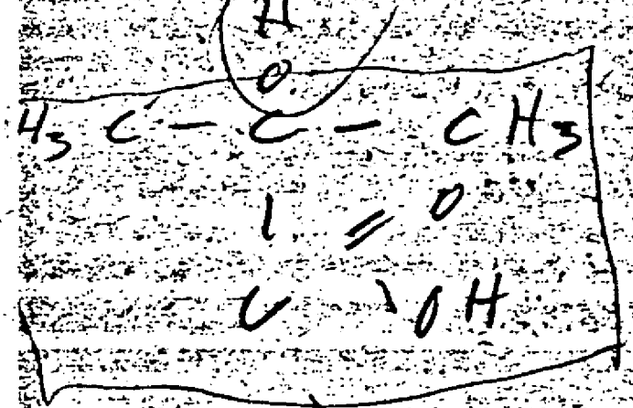
ester


Cl
H3C — C — CH3
O
C — OH
PCl3

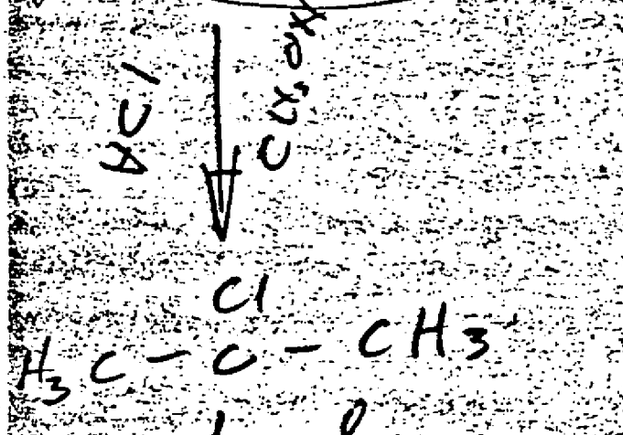

Cl
H3C — C — CH3
O
C — Cl
+
CH3OH
2HCl
+
salt

Ch. II

1. oxidation of carbinols to isobutyric acid molecule



$\xrightarrow{CrO_3, OH}$

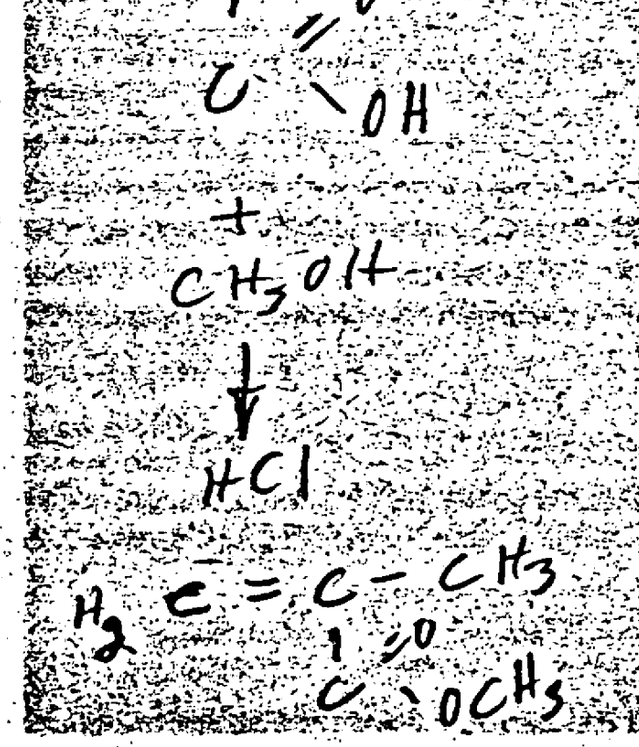


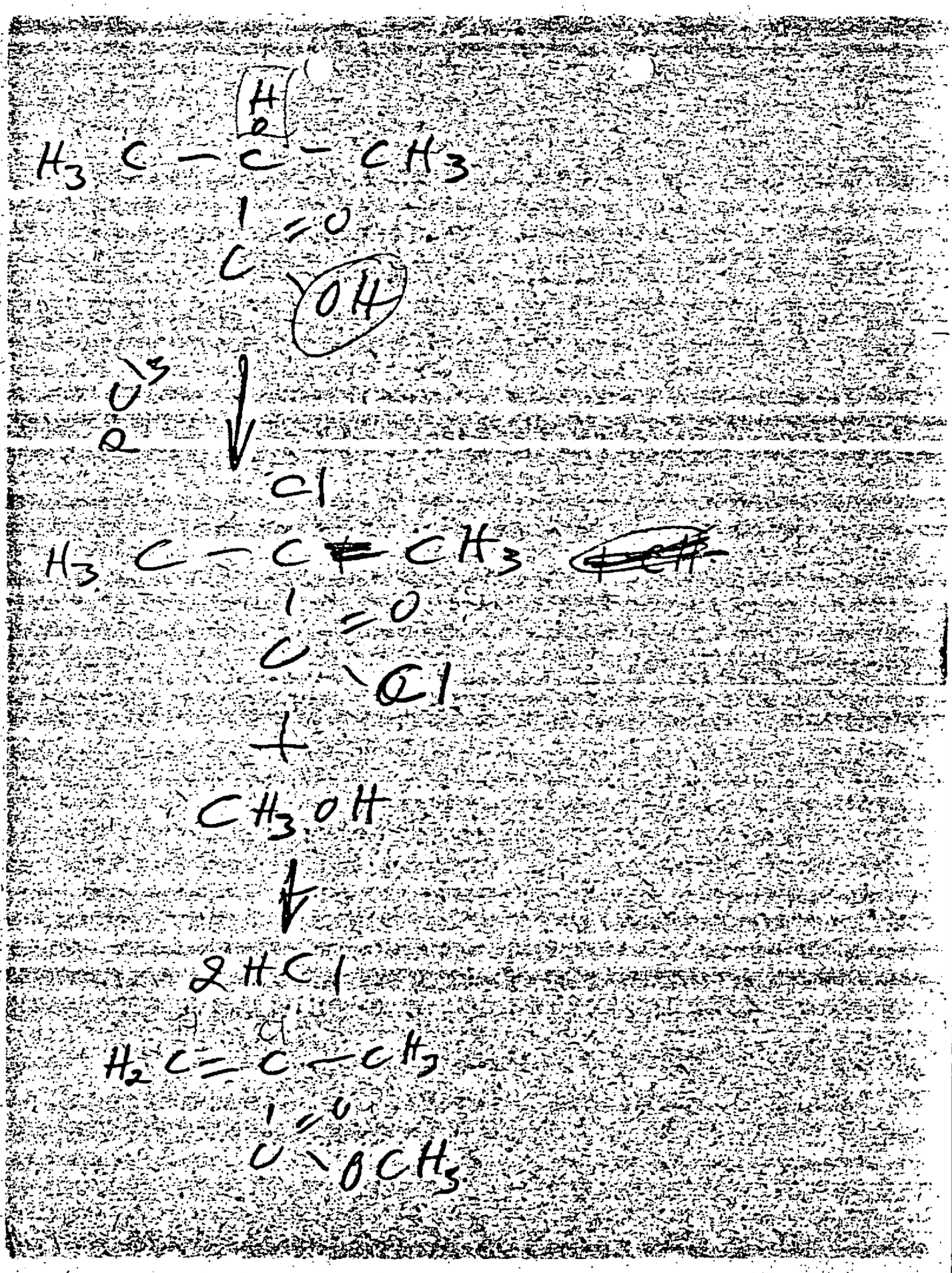
+

CH_3OH

$\downarrow$

HCl




H
H3C — C — CH3
C=O
OH
PCl5
Cl
H3C — C — CH3
C=O
Cl
CH3OH
2HCl
Cl
H2C = C — CH3
C=O
OCH3

$$2.303 \log \frac{100}{76} = \frac{994 \times 84}{1.986}\left[\frac{1}{369} - \frac{1}{T_1}\right]$$

$$2.303 \times (-0.284) = (4.19\times10^3)(2.71\times10^{-3}) - \frac{4.16\times10^3}{T_1}$$

$$-2.15\ T_1 = 11.39\ T_1 - 4.16\times10^3$$

$$\frac{11.39}{13.44}\ T_1 = 4.16\times10^3$$

$$T_1 = 309\,K$$

$$t_1 = 32^\circ C$$

$$\frac{10.000}{3.121} = 10$$

$$\frac{994 \times L}{369} = 2.7$$

$$L = 99.4$$

$$\frac{1002 \times L}{471} = 2.7$$

$$L = 75.4$$

$$2.05\ T_1 = \frac{75.4 \times 1.02}{1.986}\left[\frac{1}{471} - \frac{1}{T_1}\right]$$

$$2.05\ T_1 = (5.39\times10^3)(2.12\times10^{-3}) - \frac{2.99}{T_1}$$

$$\frac{2.05\ T_1}{11.42} = \frac{8.99\times10^3}{11.42}$$

$$T_1 = 401\,K = 128^\circ C$$

(1) Select a temp. – some – at 100 —,

(2) at that temp ~~[illegible]~~ ~~[illegible]~~ calc V.P of liquid & solids

(3) From Raoult's calc what liq. V.P.s are in soln.

add all if they come to 200

(4) $\frac{m \cdot H}{T_b}$ (g/mol, cal/g, °K) $= 22.7$ $\qquad T_b$ = "normal" b.p °K

$$-.303 \log_{10} \frac{200}{760} = \frac{H \cdot m}{1.986} \left[\frac{1}{T_b} - \frac{1}{T_1} \right]$$

(H in cal/g, m in g/mol; 1.986 cal/g mol °K)

6/6/50