Distillation of Me-Me Run — 0 3/22/47

Time	Bath Temp	Still Pot Temp	Low Column Temp	Top Column Temp
12:44	143°C	102°C	75°C	67°C
12:47	149°C	106.5°C	78°C	69°C

Take first cut at 69.5°C, time 1:48.
Cut = 7.5 g.

Time	Bath Temp	Still Pot Temp	Low Column Temp	Top Column Temp
12:52	157°C	111°C	83°C	70.7°C
12:58	165°C	120°C	88°C	72°C

Interruption

Time	Bath Temp	Still Pot Temp	Low Column Temp	Top Column Temp
1:20	175°C	133°C	88°C	(66°C)
1:25	189°C	137°C	102°C	73°C

Begin steam distillation
Phosphoric Acid formed by original steam.

Time	Bath Temp	Still Pot Temp	Low Column Temp	Top Column Temp
1:45	110°C	112°C	94°C	(No Column)

Add 20 cc water

Time	Bath Temp	Still Pot Temp	Low Column Temp	Top Column Temp
1:57	112°C ~~105~~	105°C	99.5°C	

Noted that 2 phase system cannot be formed. Therefore steam distillation cannot be run. We project a stripping operation, heating still pot & passing steam through.

Time	Bath Temp	Still Pot Temp	Low Column Temp	Top Column Temp
2:12	149°C	106°C	100°C	

3-22-41

6. 8:22 Begin to heat reaction mixture for reflux.

7. Reflux Temperatures

Time	Temp.	Observations
8:40	64°C	not refluxing, solution homogeneously black.
9:05	91°C	Refluxing Slight reflux began at 86°C.
9:10	93°C	
9:15	94°C	Remove water bath & replace with oil bath. This interrupts reaction until 9:35
9:37	90° C	Refluxing begins again Low temp probably due to methanol from condenser during shutdown
9:40	94°C	
9:42	95.5°C	
9:57	96°C	reaction seems over
10:00	97°C	
10:35	98° C	
11:15	98.5°C	
11:55	98.8°C	

Run #7. O 2-19-47

Distillation (Vacuum [illegible] [illegible])

Time	Still Pot, °C	Lower col °C	Upper col. °C	Press.	Notes
[illegible]	29	26	25	100	
[illegible]	29	26	25	100	
[illegible]	29	26	25	100	
[illegible]	29	26	25	100	
[illegible]	29	27	26	100	
[illegible]	29	28	26	100	
[illegible]	30	29	27	100	
[illegible]	30	29	27	100	
[illegible]	31	30	27	100	
[illegible]	32	31	28	100	
[illegible]	35	33	30	100	cut
[illegible]	35	34	30	100	
[illegible]	38	36	34	100	no boiling in Still!
[illegible]	40	38	36	100	boiling again
[illegible]	44	42	40	100	
[illegible]	52	49	45	100	cut
[illegible]	—	45	42	60	
[illegible]	—	46	43	60	
[illegible]	—	46	44	60	

6/6/50

23
9
16.5
17.5
14.5
17.2
97.7
19
78.7

Sholem

Silverstein

Glen McGlone

Leo Vanaman

Sy:-

Repeat last run of esterification with identical quantities as per previous run, with the following differences:-

a. employ fraction #2 of last run + sufficient of fraction #1 to make up to 64 gms. of "methanol"*

---

* remove 16 gms. of "methanol" charge & saturate with HCl

"methanol"

80.4 = tol
64
144.4

16 gms.

154.2
16
170.2

232.1
55.1 = ring
177.0

Na₂SO₄

232.1
15.1
247.2

x-acid

296.2
52
348.2

80.1
118.3
198.4
231.1
517

37

19.

2(HCl)

V₂O₅

2-1878

esterification with PCl_3

__Trial__

39 mm. α-OH acid

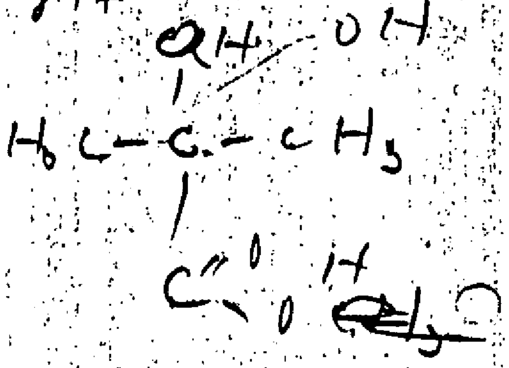
34.4 mm: PCl_3

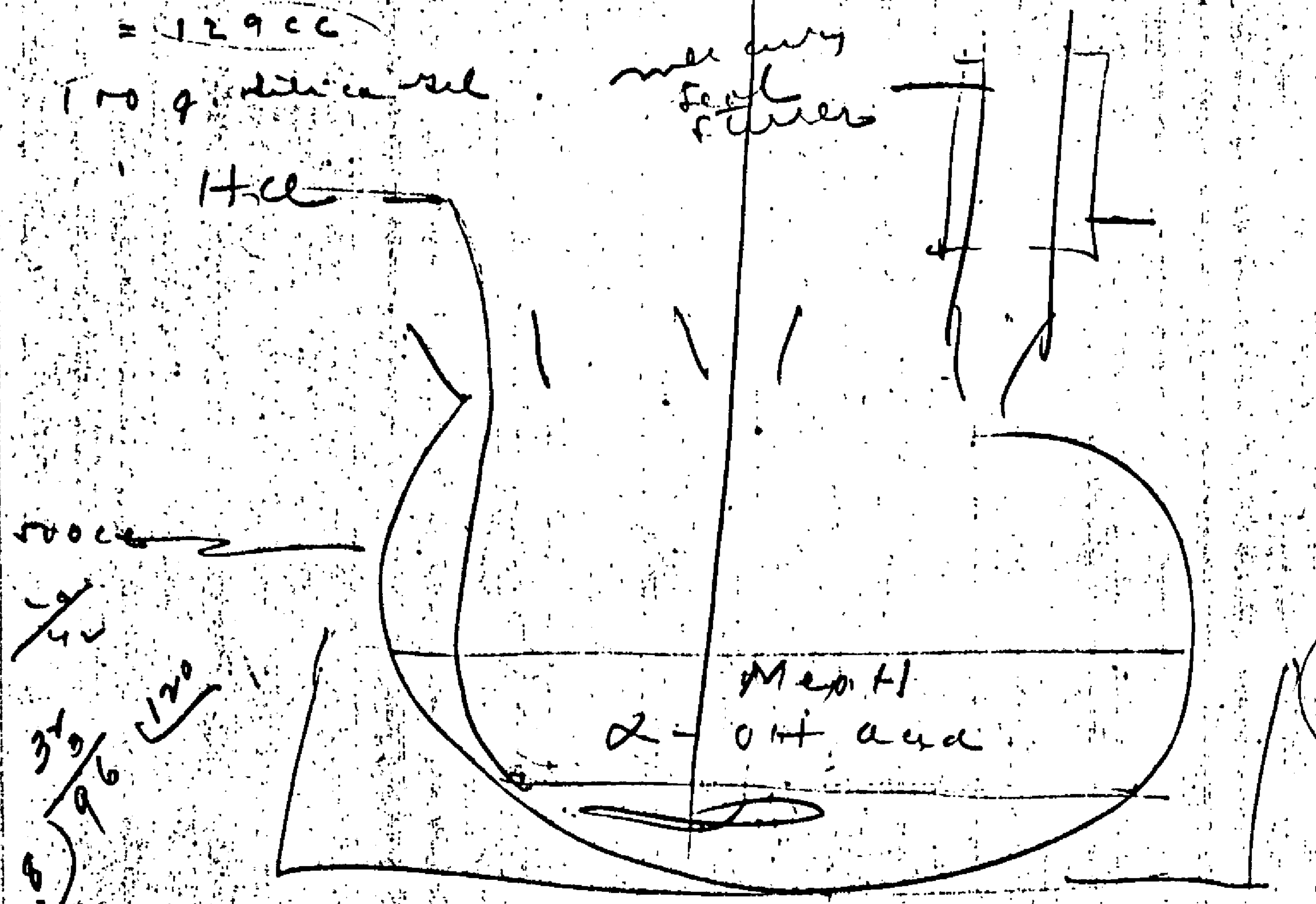
add acid to PCl_3 – No visible reaction

3 moles of MeOH
= 129 cc

100 g silica gel.

4 C 48
3 0 47
8 H 8
108/ 135





1 hr

Low Temp.
~5°C

9/44

3.9/96 120

8

108/3

4) 31.2/78

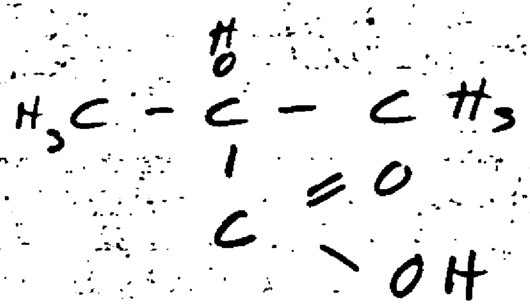
4 moles : 1 mol
1 hr HCl
4 hrs at R.T.
2 hrs at 50-60°C

78 gms. α-OH isobutyric acid

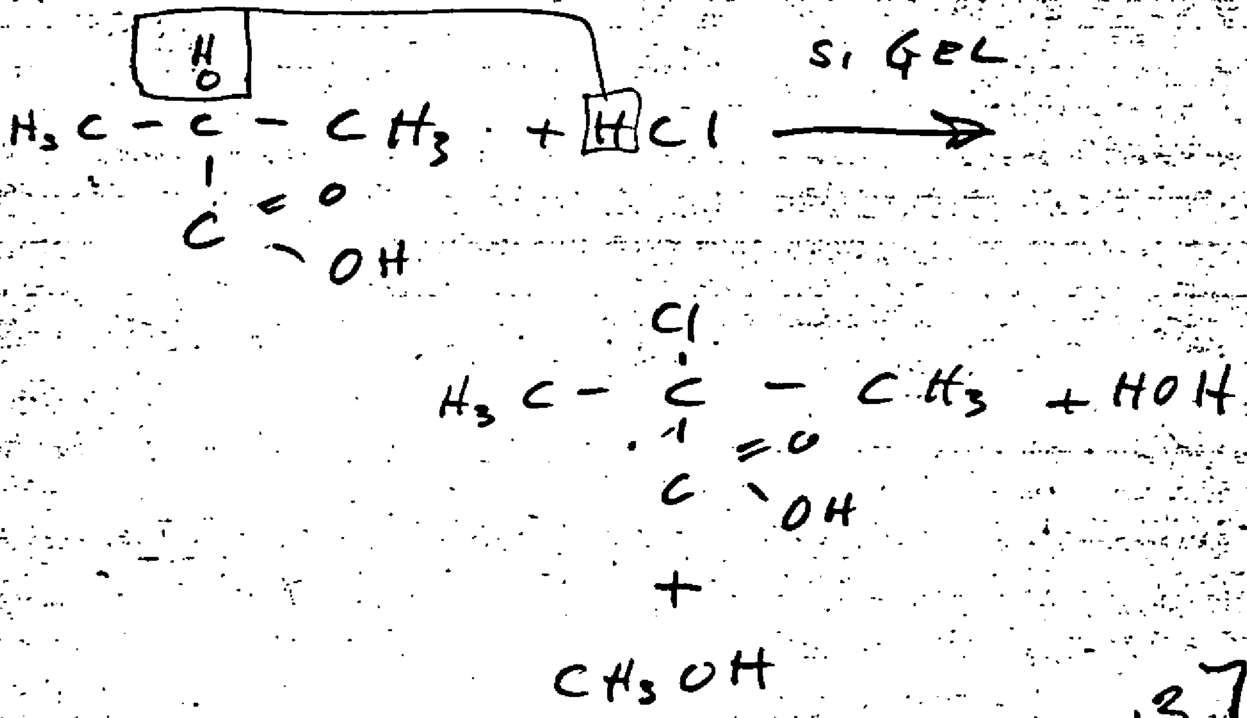
4:1 mol ratio methanol to acid

100 gms. silica gel

6/6/50

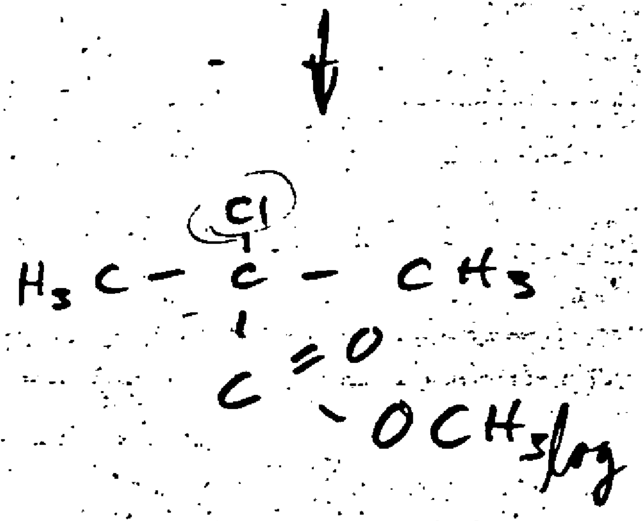


HO
H3C – C – CH3
C =O
OH

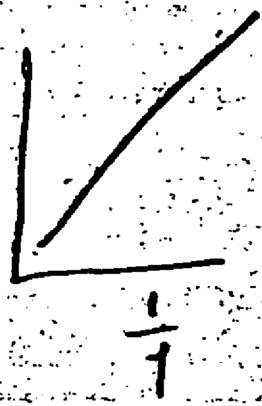


HO
H3C – C – CH3
C =O
OH
+ HCl
Si GEL
Cl
H3C – C – CH3
C =O
OH
+ HOH
+
CH3OH

137
133



Cl
H3C – C – CH3
C =O
OCH3
log



1/T

Total to be distilled 55.0
245.0
300 g

	Bath	In Flask	Bottom of Col	Top Col	Press
12:00	56	36	30	24½	100
25	75	39	34	26½	100
32	78	41	36½	29	100
35	80	40½	"	31½	100
40	81	41	37	32½	100
50	84	42	39	34½	"
1:00	86	44½	40½	37	"
13	92	46	42½	39	"

First cut up to 39° = 89.5 g

2:00 Resumed distillation

20	92	49	44	41	100
30	91	51½	47½	44	"
40	94	52	49	45	"

Second cut 51 g

3:00	100	56	53	49	100
10	115	57	55	51	"
20	115	59	56½	52½	"
30	117	62	59	54½	"
40	119	70	62	57	"
55	118	91	62	41	50
4:00	120	100	64	35	50

(No distillation)

Third Cut = 102.9

Residue 53.1

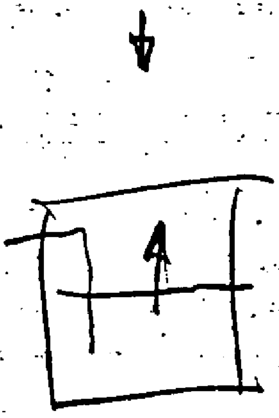
89.5
51.0
102.9
53.1
296.5

727
760
[illegible]67
760
[illegible]93

191.6
28.
219.6

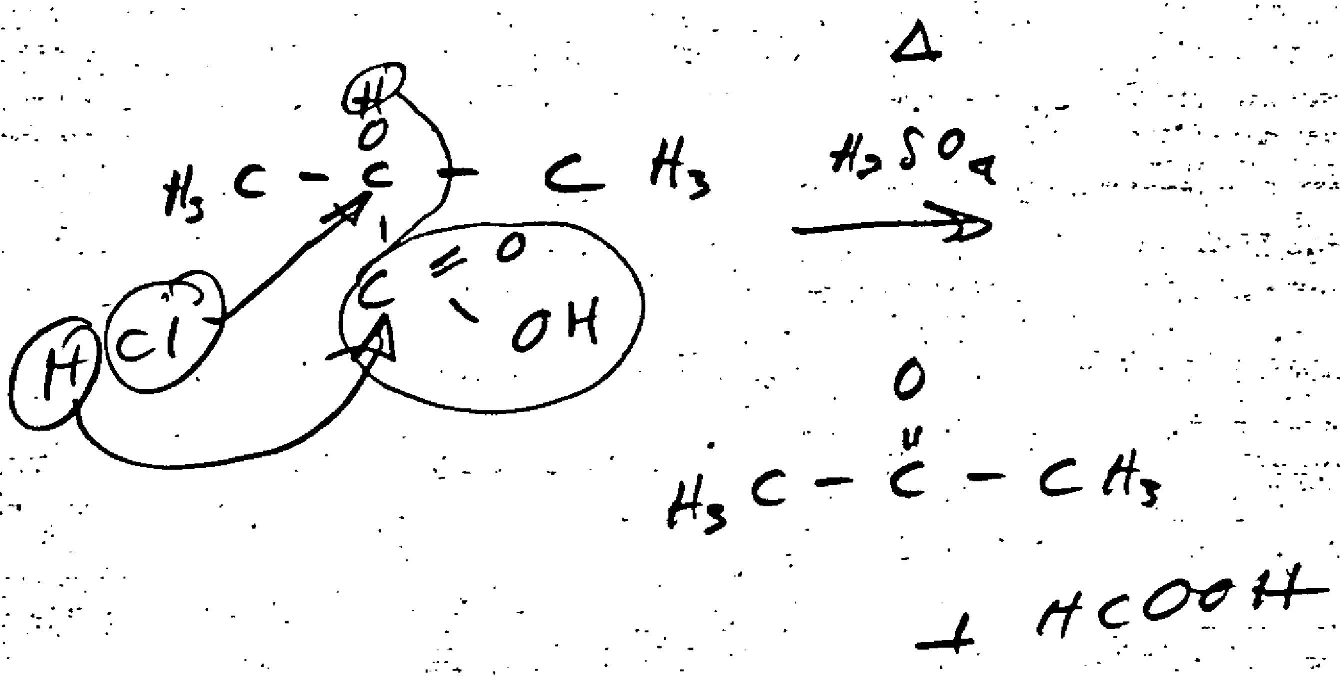
< 75 , 75-100 , 100-108°

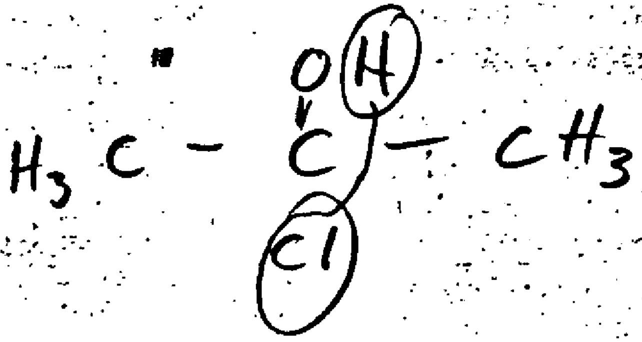
methanol

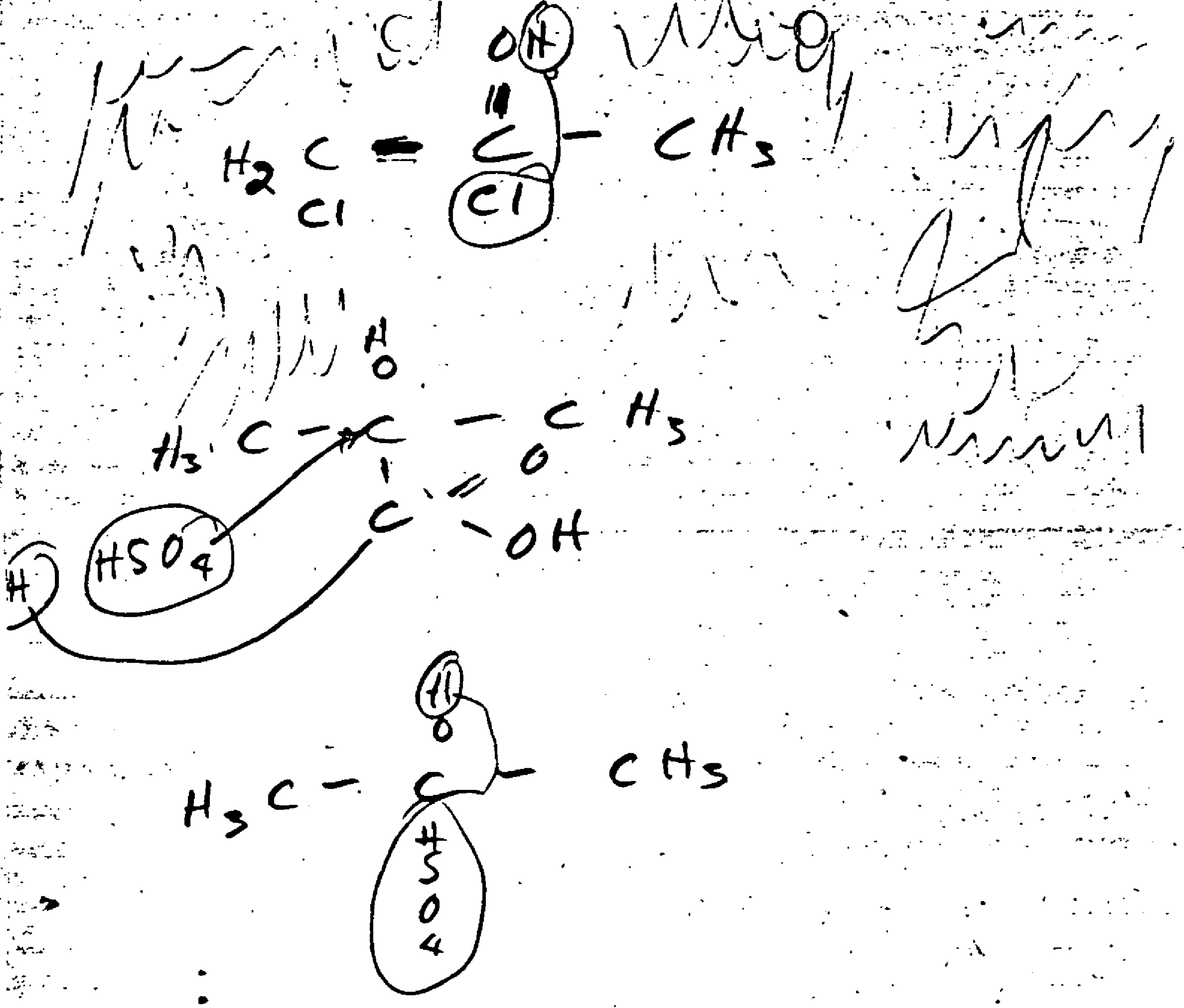


v.p. gas

v.p. liquid >






H₂C = C – CH₃
Cl
OH
Cl
H₃C – C – CH₃
HSO₄
H
OH
H₃C – C – CH₃
HSO₄

$150 + 273 = 423°K$, $\frac{1}{T} = 0.00236$

v.p. methanol = 11,000 mm. Hg.
v.p. acid = 70 mm. Hg.

for a molar ratio of 4 mols of alcohol to 1 mol acid

$$\frac{4\,(70)}{1\,(11{,}000)} = \frac{1}{39.3}$$

This would use a π of :-

$$\frac{1}{40.3}(11{,}000) + \frac{39.3}{40.3}(70) = 273 + 68 = 341 \text{ mm}$$

—— // ——

$125 + 273 = 398°K$, $\frac{1}{T} = 0.00251$

v.p. methanol = 5800 mm
v.p. acid = 23 mm

$$\frac{4\,(23)}{1\,(5800)} = \frac{1}{63.1}$$

$$\frac{1}{64.1}(5800) + \frac{63.1}{64.1}(23) = 90.5 + 22.6 = 113.1 \text{ mm}$$

$175 + 273 = 448°K$, $\frac{1}{T} = 0.00223$

v.p. methanol = 15,400 mm
v.p. acid = 21.5 mm

$$\frac{4\,(21.5)}{1\,(15{,}400)} = \frac{1}{17.91}$$

$$\frac{1}{18.91}(15{,}400) + \frac{17.91}{18.91}(21.5) = 81.5 + 203.8 = \underline{285.3}$$

$\boxed{2\ C_2H_2} \longrightarrow 1\ CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

$\boxed{26}$ ~~58~~ $\boxed{29\ g}$

$\frac{29}{26} \times 19$

M.W.

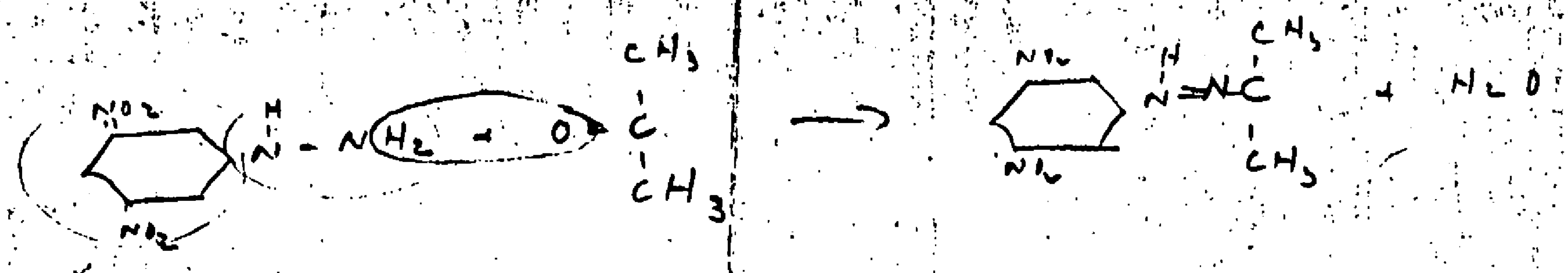
$\text{liters} \propto \frac{273}{293} \times \frac{\boxed{26}}{\boxed{22.4}} =$

$2\ C_2H_2 \longrightarrow 1$ acetone

52 58

26 29

6/6/8



$$\frac{16.5}{22.4} \times \frac{273}{293} \times 26 =$$

C_6H_{12} → 2 acet

6 → 29

1.7.8 →

$$\frac{187}{199}$$

58.1
198.1

256.2
18.1

238.2

18.7 g acetone $\frac{58.1}{238.2}$ = 0.244

19.9 ~~thio~~

$$\frac{111.4}{2.552} \times 0.429$$

1.459 = 0.429 g. acetone

= ~~[illegible]~~ acetone

18.7 g

1-28-46

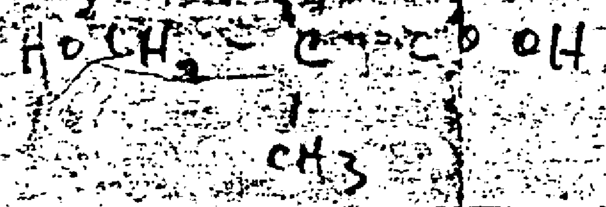
Methanol azeotropes

Substance	B.P. °C	mole % CH_3OH
[illegible] $C_2H_4Cl_2$	49.0	28.5
EtOAc	62.3	91.7
Methylcyclohexane C_7H_{14}	60	89
[illegible]	58.3	61.4

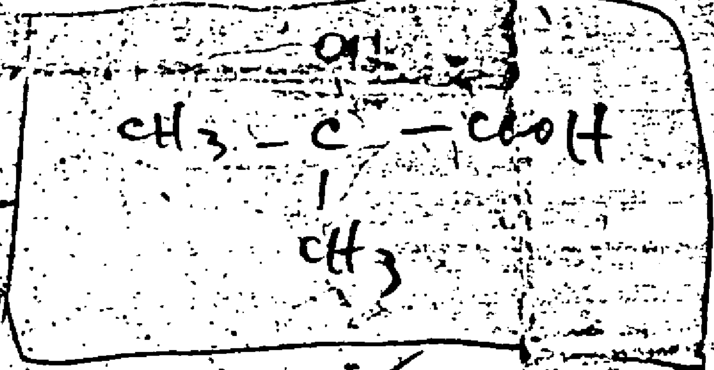
	mole %	B.P. °C
C_2H_5OH	22.9	64.9
C_6H_6	53.9	
H_2O	[illegible]	

Solubility °C	[illegible] H_2O	[illegible] C_2H_5OH	[illegible]
0 [illegible] CCl_4			
0.97	0.14	0.74	1.13
0.40	0.60	1.79	0.93
0.20	0.90	[illegible]	0.7

1/6/50



$HOCH_2-\underset{CH_3}{C}-COOH$



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

188

188

Crime and Industrial
27 [illegible] 1950
Paul Hatt
a new book [illegible] for [illegible]

1/6/50

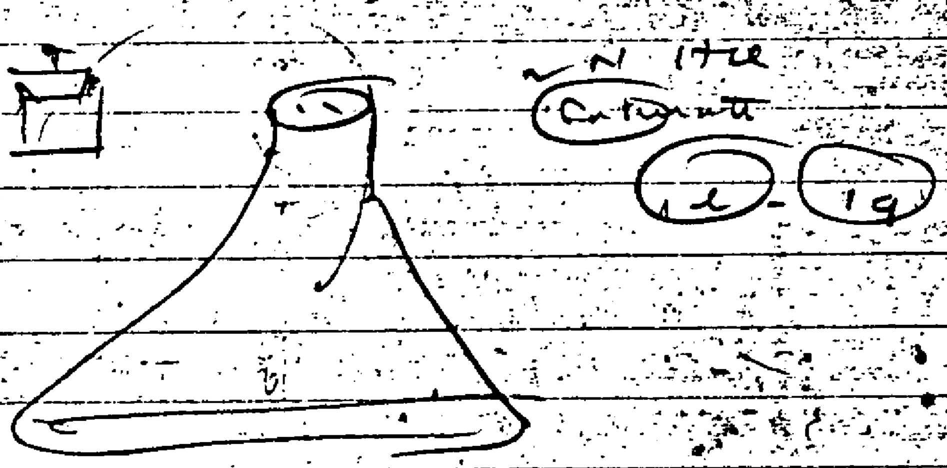
A. BROTHMAN & ASSOCIATES

No. of
Date:
By:

JOB:
SUBJECT:

(20.70) and 1 [illegible]
use smaller sample

1. 2-3 g. Sample
2. add PhNH soln: 200 cc (if more)
3. cool to 0°C ... [illegible]
4. Filter
5. Treat Filtrate with 1 g (mm) cc PhNH: soln
cool, etc
6. Filter off ppt. & Dry (45°C) - overnight
7. Repeat using total PhNH needed in one shot.
9 [illegible] - use just right amt of reagent.



2-24-47

0.975 Hr [illegible]

[illegible] Na_2SO_4 [illegible] H_2O

x = [illegible] 0.975

$\frac{0.975}{7} \times 142 =$ 19.8 [illegible]

[illegible] .99 $\boxed{I}$

[illegible] $\boxed{29.7}$ [illegible]

[illegible]

looks like wax $\boxed{II}$

[illegible]

9.35 [illegible]

1/6/50

2-24-47

Esterification of α-OH Isobutyric acid

Purpose:- repeat run of 2-11-47 using triple quantities

Procedure: 2-11 = [illegible]

[I] Quantities:

4:1 mol ratio of methanol to acid {
156 gms. α-OH isobutyric acid - 1.5 mole
192 gms. methanol - 6.0 "
[Dried over $CaSO_4$]
45.3 gms anhydrous Na_2SO_4

[II] Procedure.

48 gms. of the 192 gms. portion of MeOH were saturated with hydrogen chloride and then added to the remainder of the MeOH. In this remainder had previously been dissolved

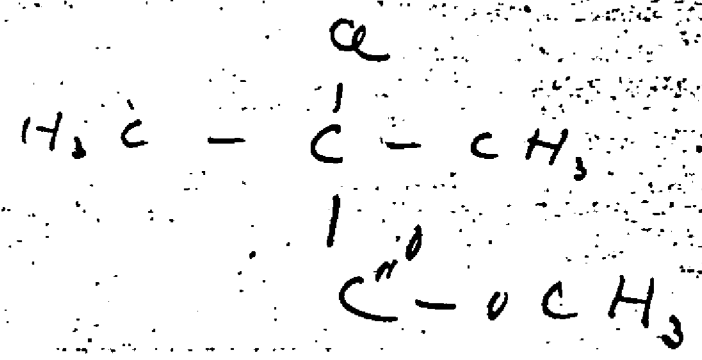
sample

0.6854
7.7727
2.9127

10.8393
7.7730
3.0663

19.7655
19.2334
.532

273.2



$$H_3C-\overset{\overset{Cl}{|}}{\underset{\underset{\overset{O}{\|}C-OCH_3}{|}}{C}}-CH_3$$

133 - 135

~~15.6[illegible]~~
~~12.3780~~
~~3.25[illegible]8~~

15.8293
12.3780
3.25[illegible]8

16.8936
16.7222
[illegible]

17.7952
16.7822
1.01[illegible]

17.7914
16.7822
1.009[illegible]

6/6/56

Silica gel 107 g

Temp (3) rose rapidly from 65 to 75

Fraction up to 75° – 31.3 g

Fraction 75–100 23.6 g

①

② 113°C

Bath 190°C

---

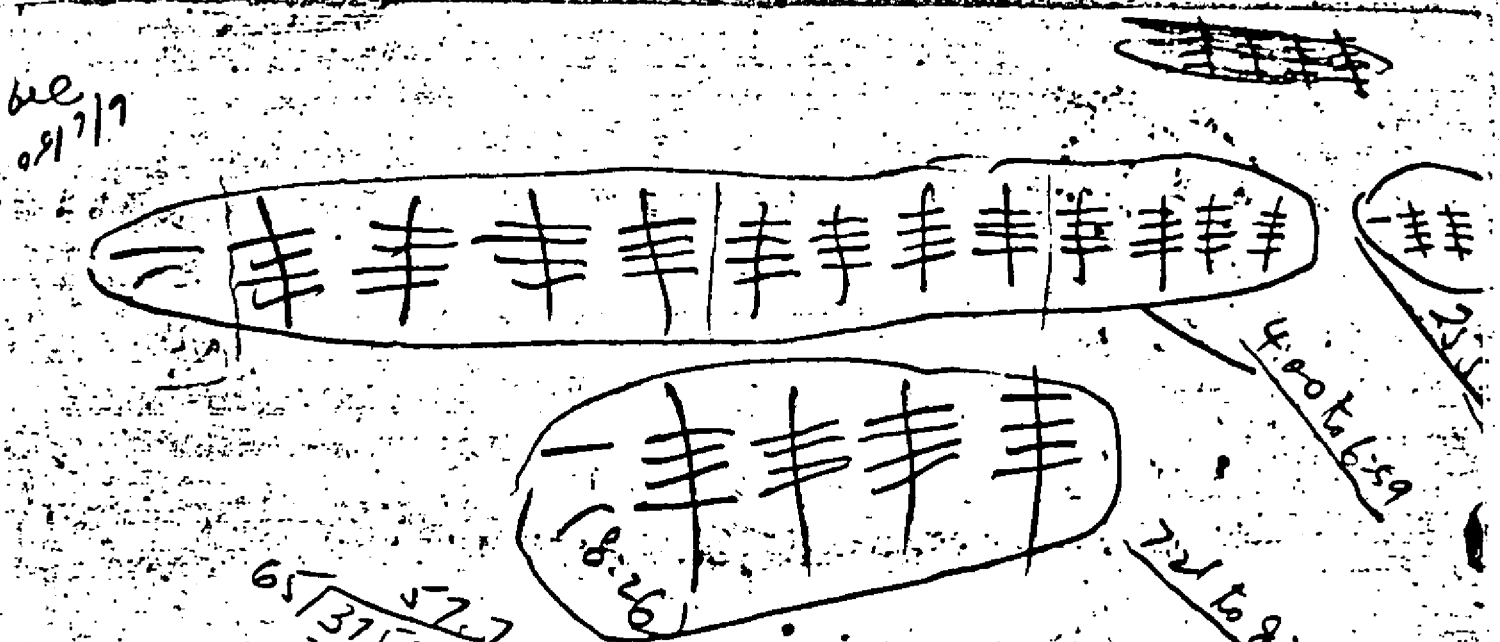
③ 108°

② 140°

① 160°

Bath 230°

6/6 150
209



25

4:00 to 6:59

7:21 to 8:26

$$\begin{array}{r} 57.7 \\ 65\overline{)3750} \\ 325 \\ \hline 500 \\ 455 \\ \hline 45 \end{array}$$

[illegible]

tare 431.4
−255.7
175.7 on chol.

243.8
165.4
78.4

Lost in Flask
−258.7
288.7
30.0 g.

Fract. #3
38.5 g. tare + flask
−24.1 g tare
14.4 g. Dry

Fract #1
170.0
80.4 Tare
89.6 g. dist.

Res. 176.8
135.4
41.4

Fract #2

141.0
90.8
50.2

50.2
11.4
14.4
76.0

22.6 g = Methyl α-OH iso-butyrate (?) a[illegible] to
22.6 g Chlorosulphonic acid with agitation at
-10 to -20° C
+ 5:30 passed over 75 g ice with 3.8 g Na_2SO_4

Found Chlorosulphonic acid in acid shelf

Machine has no Zn Vernier, but will make [illegible] order ~ 10 [illegible] 1.15 Q.
10 days

253.8
72.6
$\boxed{181.2}$

ask

3.8
18
21.8

356.1
15.1
$\boxed{371.2}$

[illegible] for [illegible] acet [illegible]

78 g

179 ml

100 g

[illegible] gel

dry HCl [illegible] 7.45

60°C

(many)

(HCl [illegible])

78

1.5

Before 12C

65-4307
Encl 12C

Nylon

Nylon - Preliminary Study

efinition -

Nylon is the name applied to the polymerization product of:

Hexamethylene diamine
and
adipic acid

thus:

$-(CH_2)_6 - -$

U. S. 2,130,523   Sept. 20, 1938   Wallace H. Carothers

Claims

$NH_2(CH_2)_nNH_2$ Diamine $COOH(CH_2)_mCOOH$ with

$m + n$ being > 4.

Specifically claims

"polyhexamethylene adipamide".

Gives method of spinning

Gives properties of fibers

U. S. 2,071,250   Feb. 16, 1937   Wallace H Carothers

Forerunner to 2,130,523.

2,130,947   Sept 20, 1938   Wallace H. Carothers

prepn of salt

2,130,948   Sept. 20, 1938   Wallace H. Carothers

claims reaction of a diamine & dicarboxylic acid

gives details of

2,158,064   May 16, 1939   W. H. C.

resins

2,361,717 Oct. 31, 1944 Guy B. Taylor

continuous method

Hexamethylenediammonium adipate

7

084.9

U.S. 1,921,101

$$\text{Cyclohexanol} \xrightarrow{HNO_3} \text{a dipic acid}$$

V or Mo oxide
or
NH_4 Vanadate
or
HgO or $HgSO_4$

50-60°

others - Dow

4. 35, 7587[11], 7588[1,2] ⑩

35, 1799[6,7]

35, 3650[8]

35, 4398[7] I.G. Farben.

34

93[5] adipic acid

$$\text{cyclohexylamine} \xrightarrow[95-100^\circ]{HNO_3} \text{adipic acid}$$

01[2] adiponitrile (unsaturated) + excess NH_3

$$\xrightarrow[\text{Ni catalyst cont'g, } 150-350^\circ \text{ for 2-6 hours}]{H_2} \text{hexamethylenediamine}$$

302[7] adipic acid

$$\xrightarrow[300-550^\circ \text{, B phosphate}]{\text{and excess } NH_3} \text{adiponitrile}$$

33

2539[2] adipic acid (gas)

$$\xrightarrow[300-400^\circ \text{, dehydration catalysts, 1-10 secs.}]{NH_3} \text{adiponitrile}$$

O.K.

---

adiponitrile $\xrightarrow[NH_3]{H_2}$ HMD.

liquid phase 75° – 200° C
press.
catalyst. Ni on Kieselguhr.
Solvent – ether, alcohol etc.
MeOH

32
9497^6 + 9498^1 — U.S. 2,130,523

Salts

Other		m.p.
pentamethylene diamine	sebacate	129-31°C
HMD	sebacate	171-2°
HMD	adipate	183-4°C
octamethylenediamine	adipate	153-4°C
"	sebacate	164-5°C
nonamethylene diamine	adipate	125-7°C

---

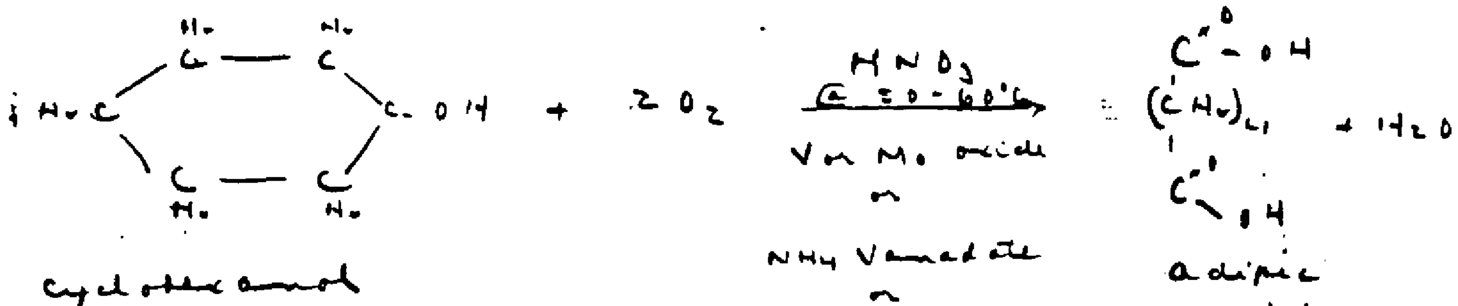
31 Homer Adkins

7884^4 aniline $\xrightarrow[press.]{H_2}$ cyclohexylamine
175-250°
Ni on Kieselguhr.

D.K.C. Lazier
31 6255^7

H_2

2.



$\mathrm{HNO_3}$ @ 50-60°C

V or Mo oxide

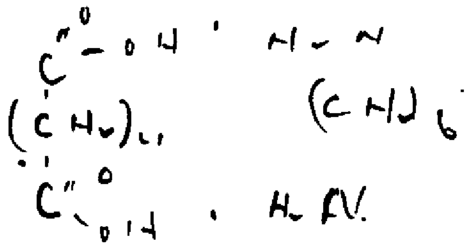
or

$\mathrm{NH_4}$ Vanadate

or

HgO and $\mathrm{HgSO_4}$

3.



$$\begin{array}{r} \boxed{260} \\ 1.8\,\overline{)\,468} \\ 36 \\ \hline 96 \end{array}$$

for HCl

con 12.5 mmols/ml

$20 \times 0.183 = 12.5 \times x$

$\frac{3660}{12.5} = x = 0.28$ mls

$12.5 \times 1 = 0.183 \times x$

$x = \frac{12.5}{0.183} = \boxed{69}$

~~0.75 M~~

$12.5 \times y = 25 \times 1.5$

$x = \frac{\overset{2}{\cancel{25}} \times 1.5}{\cancel{12.5}} = 3$

1.048
$\times 1.048$
8384
4192
10480
1.098304

$1250 \overline{)366088}$ $.293$
2500
11600
11250
3500

6/6/50

H_3PO_4 — $K_1 = 1.1 \times 10^{-2}$

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^=$$

$$\frac{[H^+][H_2PO_4^=]}{[H_3PO_4]} = 1.1 \times 10^{-2} = K_1$$

$$[H^+] = [H_2PO_4^=]$$

$$[H^+]^2 = K_1 \times [H_3PO_4]$$

$$[H^+] = \sqrt{K_1 [H_3PO_4]}$$

```
 1.048
 1.048
        1.7
  332   1.7
  332   119
        17
  6.64  √3.5
  996
 998
1.0224
```

$[H_3PO_4]$ = 300 mmols/100 mls

= 3 mmols /mls

$$[H^+] = \sqrt{(1.1 \times 10^{-2})(3)}$$

$$= (1.05 \times 10^{-1})(1.73)$$

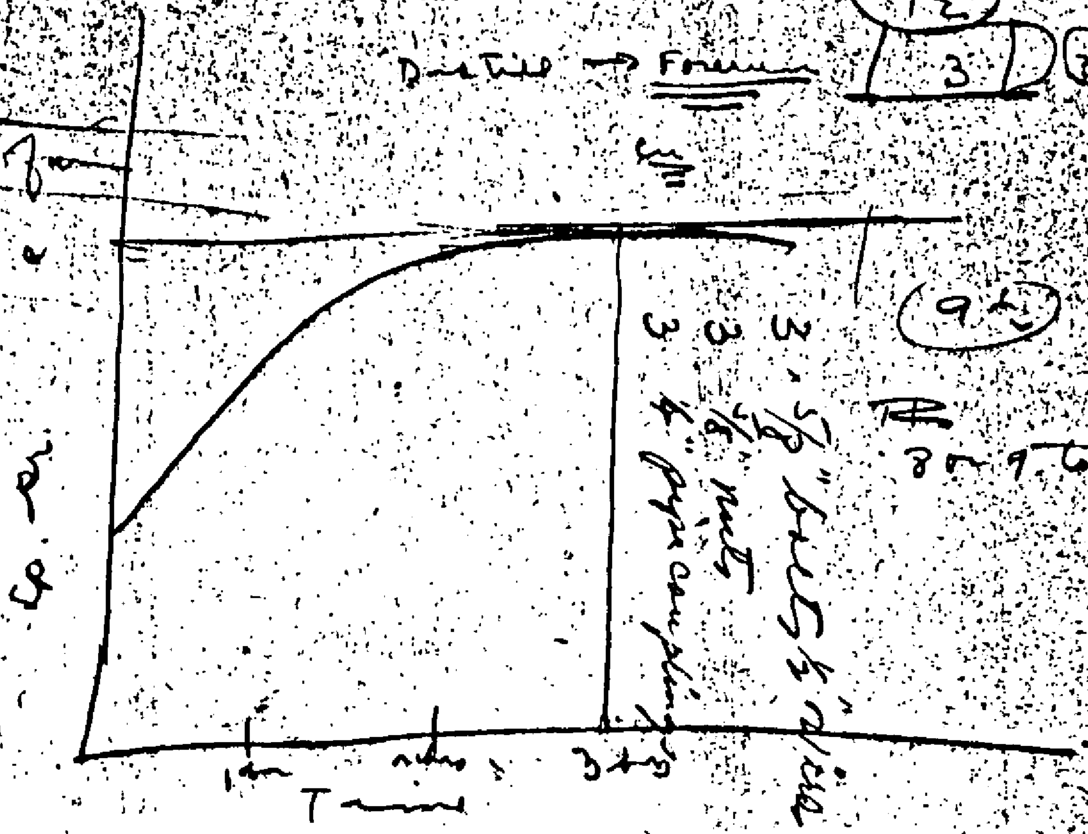
$$= 0.105 \times 1.73 = 0.183 \text{ mmols/mls}$$

25 hrs
3 hrs
~~4 hrs [illegible]~~
8 hrs

$\boxed{17.5}$

Ductile → Forming

(1 1/2) 3 (3 1/2)



3 - 5/8" bolts 1/2" wide
3 - 5/8" nuts
3 - 4" pipe coupling

(9 1/2)

8 or 9 [illegible]

C O

1. temp 30-45°
stay close to 30° then 35
if it will polymerize
particularly well in HCl
30-32°

2. keep system at R.T.

3. after all HCl has been added continue until no appreciable rise in reaction

Sp. gr. vs Time plot

3 hrs

after plateau in reaction make acid with 1N HCl,

4. Keep on during distillation
[illegible]

Nylon — C.A. 1945

References

Textile J. Australia 19, 236-8.

Loom 4, 461-4.

Chem & Met. 52, no. 8, p. 94-7 (1945)

Chem & Met. 52

Benzene → phenol $\xrightarrow{H_2}$ cyclohexanol

$\xrightarrow{O_2}$ cyclohexanone $\xrightarrow{O}$ adipic acid

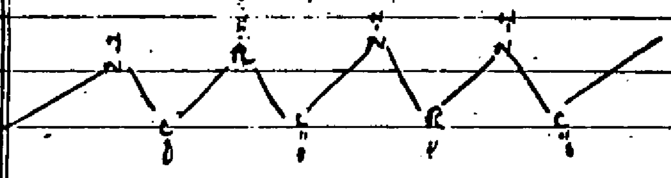
$\xrightarrow{NH_3}$ adipamide $\xrightarrow{-H_2O}$ adiponitrile

$\xrightarrow{H_2}$ tetramethylene diamine

$n\ H_2N(CH_2)_6NH_2 + n\ HOOC(CH_2)_4COOH \rightarrow$

$[NH(CH_2)_6NH-\overset{O}{C}-(CH_2)_4-\overset{O}{C}-NH(CH_2)_6NH]_n\ (2n-1)\ H_2O$

polyamide



Mix hexamethylene diamine & adipic acid

→ equivalence point at pH 7.63

Usually, do not prepare polyamide directly from diamine & adipic acid but prepare & isolate the diamine dicarboxylic acid salt as an intermediate in the polyamide formation. This eliminates the impurities in the starting materials & eliminates the difficulty of purifying the starting materials in a state of purity.

Hexamethylene diammonium adipate is conveniently prepared in hot ethanol by mixing solns. of the diamine with approximately an equivalent amount of the acid (U.S.P. 2,130,947 - 1939 - Carothers).

and adjusting the neutralization point.

A mixt of 144 parts of HMD, 174 parts of adipic and [illegible] parts of 95% ethanol & 210 parts of H_2O are warmed until completely dissolved. The mixt is then cooled which causes sep. of the less soluble salt in the form of white crystals. The salt is separated by filtration & recrystallized from 1400 pts. of 95% EtOH & 200 parts of H_2O yielding [illegible] parts of the pure salt with the m.p. of 183–184°C.

This salt formation is apparently used in the commercial process (I & EC. 34, 63 (19[illegible])). Another patent (U.S. 2,130,948 W.H.C. – 1938) describes the formation of the fiber forming polyamide from the salt which may be carried out by heating the salt in bulk, in a solvent or non-solvent.

In the first method the salt may be heated in the absence of a solvent or diluent to 150–300°C under conditions permitting the removal of the water formed.

Two moles of HMD adipamide & 0.12 mole of adipic acid (viscosity stabilizer) are placed in a 2 L silver lined autoclave equipped with a stainless steel stirrer and reflux condenser. The air is removed by evacuating, filled with N_2 & again evacuated. Then 30 psi N_2 pressure is put on the autoclave, the stirrer started and the temp. raised to 288°C over a period of 1.5 h. Pressure is decreased during 30 mins to atmospheric pressure & heating and stirring continued for 2.5 hrs longer. Then the press. is decreased to 400 mm for [illegible]. After cooling the polymer is removed from the autoclave as a white solid.

UL150
[illegible]

reactions. The O₂ content must first be lowered to less than 0.05%. This can be done by washing the [illegible] N₂ with a NaHSO₃ soln.

In 1944 a patent (U.S. 2,361,717 - 10.31.44) was granted to carry out these reactions in a continuous process. By this new process, polyamides can be prepared by continuously passing an aqueous soln. of a diamine dicarboxylic acid salt at superatmospheric pressure thru several reaction chambers at the temp. for polyamide formation. Now successful ???

In the commercial process

I & E.C. 34, 53 (1942)

I & E.C. 32, 1510 (1940)

the molten polymer after being discharged from the reactor, is extruded as a ribbon onto a chilled roll & cut into small chips. In this form the polymer is completely stable, has a crystalline structure & m.p. of 499°F. It can be stored in granular form known as "flake" for further processing. For the extrusion, the flake is charged onto a hopper of the spinning unit, dropped to a heated grid where the polymer melts & after metering & filtering is extruded into filaments. During this process the polymer is surrounded by an inert gas to avoid oxidation. The filaments harden & are wound on the bobbins at a speed of 2500 ft/m

①

Secondly – The salt may also be heated in an inert solvent for the polymer such as cresol, phenol, xylenol or diphenylol propane. When the reaction has proceeded far enough to give a polymer of good fiber quality, the solution can be removed from the reaction vessel & used as such for spinning or the polymer can be isolated by precipitation with a non-solvent.

Third – The salt may be heated in the presence of an inert non-solvent for the polymer, such as the high-boiling [illegible]. Exclusion of air during the reaction is important to prevent oxidation, which causes discoloration of the product. In general, no catalysts are needed for the reaction. However, the surface of the reaction vessel has some catalytic action & small amounts of catalysts such as oxides, carbonates & aluminum chloride are beneficial.

// Commercially, polymer "66" is apparently manufactured without any solvent or diluent, the above example providing a good example of the process most likely used. In 1939, a patent (U.S.P. 2,163,584 – A. W. Larchar) was granted for the production of light colored polyamides in reactors suitable for large scale production. The reactors are constructed of, or lined with, Ag, Tantalum, Cr steels or Chromium & are used under oxygen-free conditions.

6/6/50 Commercial N_2, with as little as 0.05% O_2 is unsatisfactory for use in these

JM

⑥

They are then cold-drawn. This stretching causes the molecules which had essentially a random distribution to orient themselves. A relatively small force is required to produce a four-fold increase in strength.

properties

Ind. Eng. Chem. 32, 1560 (1940).
Chem & met. 51, 1[illegible] (1944).

Type Nylon Yarn	Strength g/denier	Elongation
Std	4.5-4.8	18-24 %
Hi-Tenacity	6.0-7.0	11-17 %

Vol. 51, — 5

Ten types are made today but polymer "66" is still most widely used.

m.p. 253° C

moderate resistance to mineral acids & [illegible]

3. Inert to alkalies, aliphatic, aromatic & chlorinated HC's, organic acids, ethers, alcohols & CS_2.

4. Solvents include phenol, cresol, [illegible] formic acid & xylenol.

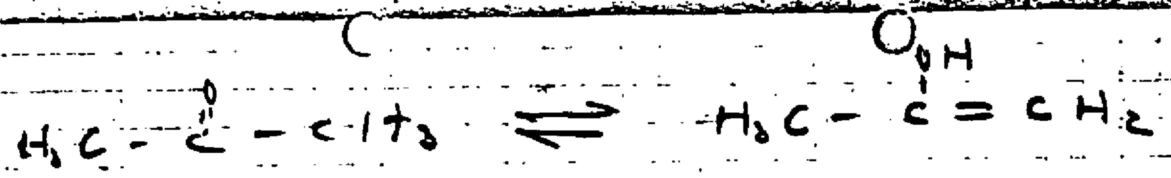
Density 1.14 — silk 1.30
viscose rayon 1.52
acetate rayon 1.30

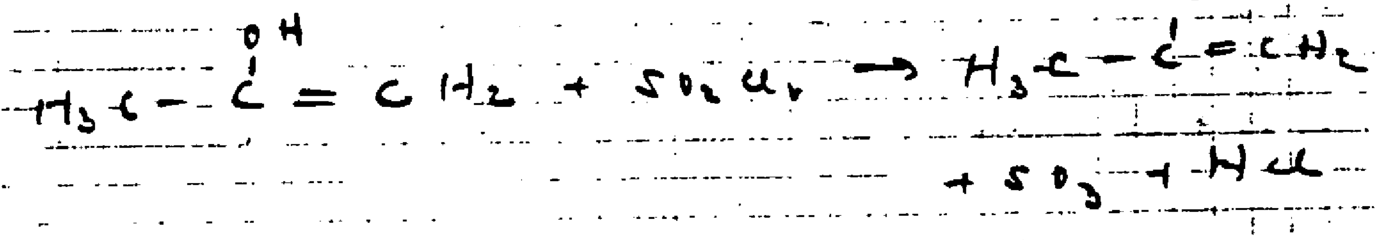
	Tenacity, g/denier	
	dry	wet
Nylon 66	5	4.8
Silk	4.5	3.9
Viscose rayon	1.7	0.9
Acetate rayon	1.5	1.0

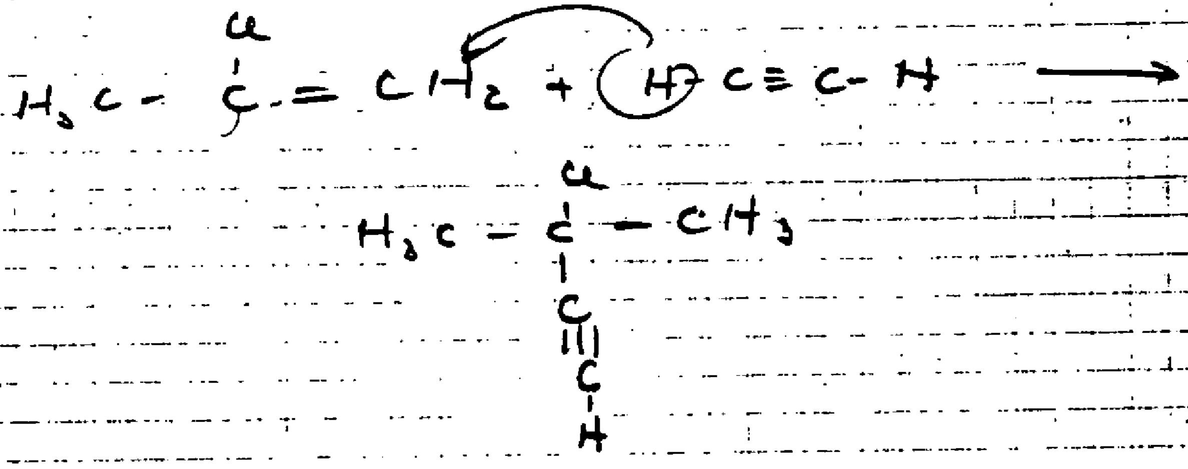
Water absorption

	Relative humidity, [illegible]		
Nylon 6/6	3.8	4.7	7-8
Silk	11		
Wool	15		
V.R.	14		
A.R.	6.5		

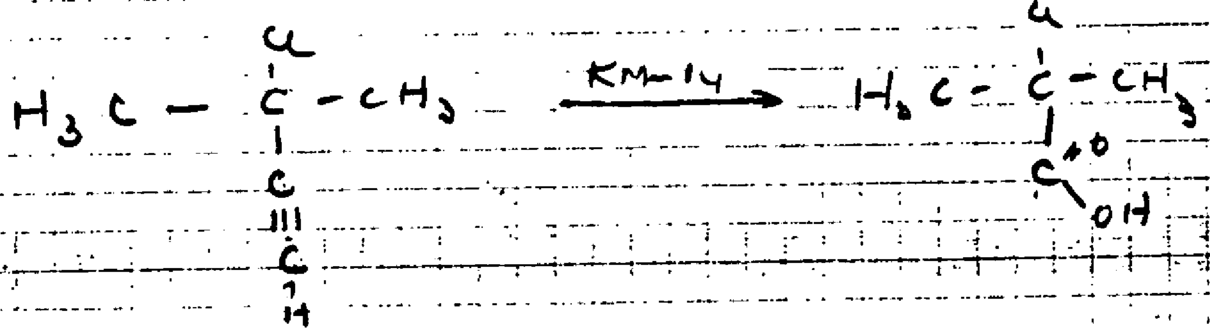
6/6/50



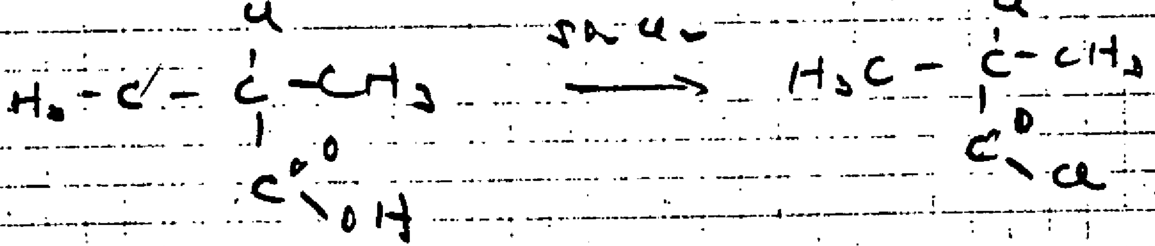




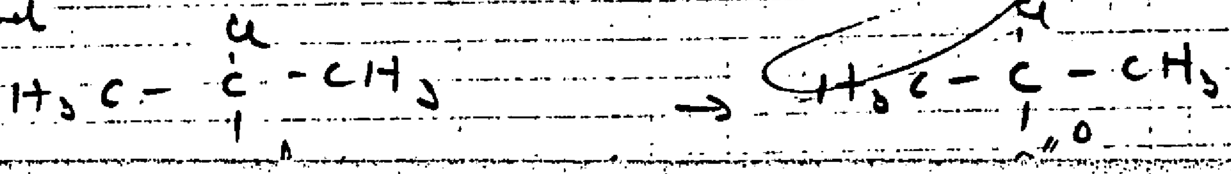
then,

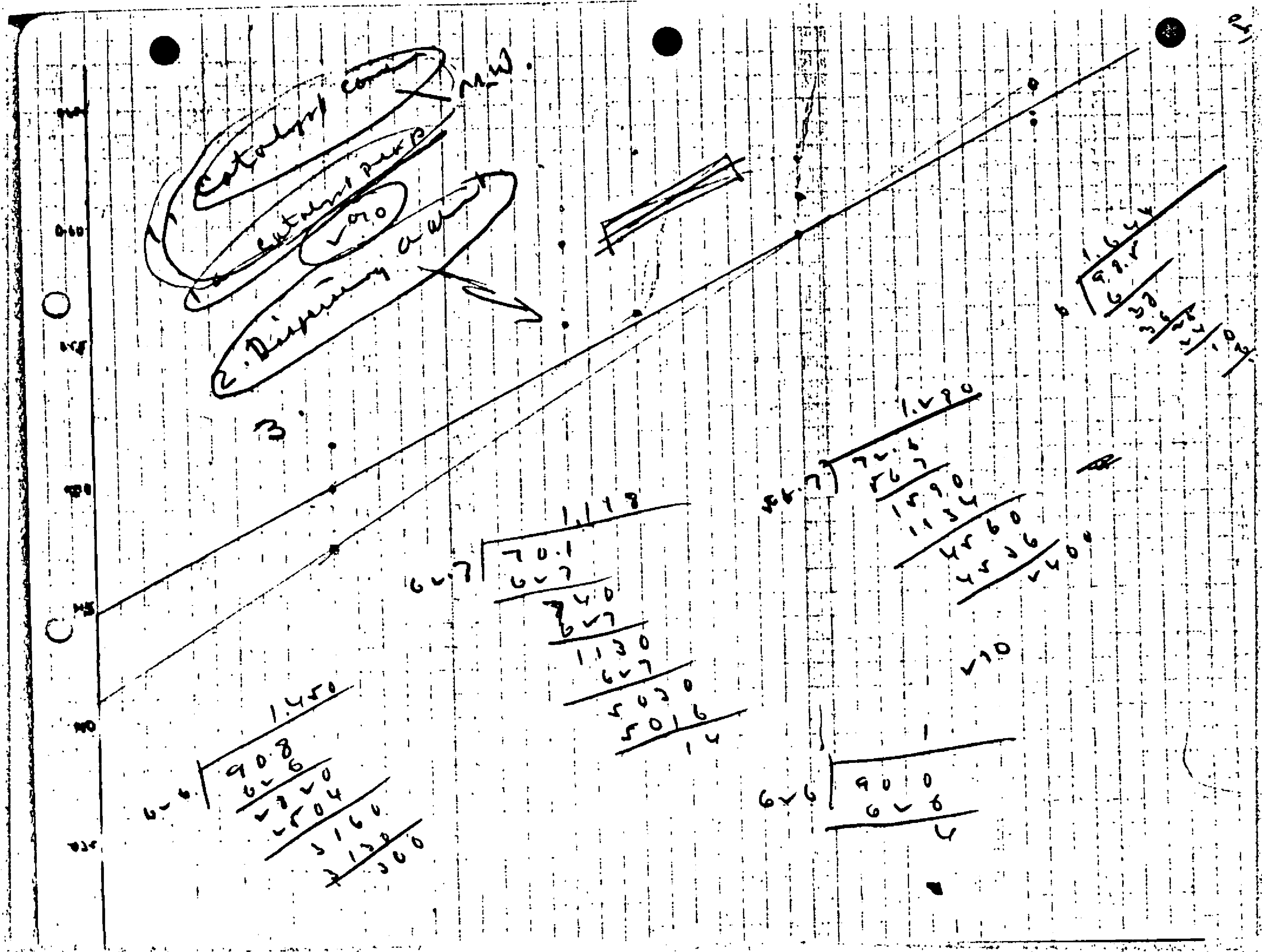


chloro, 3,3-dimethyl - [illegible] -1



and





2

Catalyst conc
Catalyst pure
20.0
MW.
2. Dispensing a weight
3.

62.6) 90.8 = 1.450
626
2820
2504
3160
3130
300

62.7) 70.1 = 1.118
627
740
627
1130
627
5030
5016
14

56.7) 72.6 = 1.280
567
1590
1134
4560
4536
240

210

6) 9.85 = 1.64
6
38
36
25
24
1.0

62.6) 90.0 = 1
628
4

9903
2716 Cure

7197

25477
7204

18273

21851
3626

25477

[illegible]

Return #1

4835
2641

2194

Return #2

17761
5004 (7714)

12757

~~50 g mono~~
~~2 g agar~~
~~1 g BP~~
~~400 g water~~
~~11.2% to~~

10-14-46
molding powder
400 cc. H_2O
50 gms.
2 " bp
0.5 " agar

Start $10^{\underline{36}}$
solution of bp in monomer stirred around for about 15-30 min before pouring into 400 cc H_2O-agar solution

$11^{\underline{00}}$ – powder appears
$11^{\underline{35}}$ – stop – seems O.K.

washed 2-3 times

~~10-9-46~~

St. A.A.

Polymer 7

243.7	191
245.35	191.6
248.2	AV. 191.3
245.5	
4 | 982.65	
AV 245.66	

more froth on filtrate

③ rinsed on paper 2-3 times – filtrate still cloudy

④ stood for about 36 hrs. under water then filtered + separated into 2 equal portions of 15.6 gms

⑤ made 1 portion with 1:5 HCl about ~~50°~~ 60° with stirring [illegible] heated the

5-120 mls
first HCl filtrate after
15 minute wash -
not milky only a
little cloudy - much
less than previous
water washes which
are opalescent

2nd wash - 10.50 -
still cloudy -
then 3 hot water
washes - all cloudy
not much diminished

5 water washes - control

//// all cloudy

54.5 | Washing Exp
75 | 10-17-46
129.5

800
.75 gm. .75
2 600.00
1.50 bp

.75
3.00 gm
ordue

cmil xo

3^{00} - powder
3^{19} stop reaction
remove bath

① washings

0,X2

457.3 457.3
12 395.8
445.3 61.8 gms. total
12.
[49.8] - left

2X 446.5
15
431.5

washings continued

thru 9X - 10/17

10/18 finished - all
washings retained

11/16 - start drying all
simultaneously

MAM

Clock - Dial

6" dial — Powder (Cube)

¼" Thickness

Press 25 sec

Drawtite plunger — W.P. 12 tons.

Kick off

Heaters { Face 600°F ~~chrome~~ + tungsten

) Rim 380°F

195°F Material chamber

Disc — Clay Display

6" dia - 7"

¼" Thickness

Du Pont line

⅜" Dia granules

press 5 secs —

Low Press — 114 secs.

Kick off

cold compressed air in press 3 [illegible]

at press 415°F

Rim 305°F

JUL 29 1946 JUL 29 1946

~~[illegible]nge.~~

[illegible] mmol

36

11

396

35

JUL 29 1946

JUL 29 1946

JUL 29 1946

JUL 29 1946

JUL 29 1946

6/6/5

brine Soln.
100 cc

← 10 cc of 2% Starch Soln

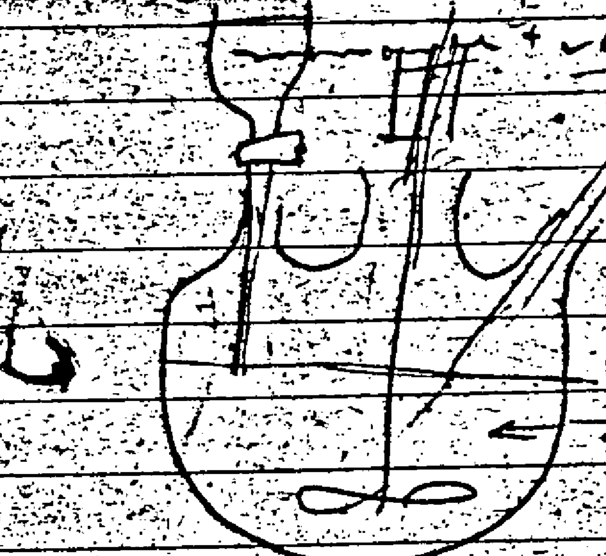
Δ

polymer & diss in acetone

then add EtOAc as diluent

~~[illegible]~~

~~[illegible]~~ + 50% EtOAc



← 2 for every 1 part of monomer add 7 parts of Soln { 2% Starch / Sat. NaCl

100 g Mon
25% CCl_4

700 cc brine Soln
70 ml of 2% Starch

~~100x~~ = ~~100 x 100~~

~~[illegible]~~

9-27-46

29

25 gms. Styrene monomer
0.5 gms. B.P.
2 gms. Gum arabic
200 gms. H_2O

Start 10:55 AM Temp. 94°C
Powder 12^{50}
Finish 1^{25}

30

25 gms. Styrene monomer
1.0 gms. B.P.
2 gms. Gum arabic
200 gms. H_2O

Start 11^{05} Temp. 94°C
Powder 12^{15}
Finish 12^{30}

9-27-46

#31

25 gms. Styrene monomer

0.25 g. B.P.

2 gms. Gum arabic

200 gms. H_2O

Start 12 55 PM Temp. 94°C

1st powd. 2 55 PM

Finish 3 40 PM

#32

25 gms. Styrene monomer

1.5 g. B.P.

2 gms. Gum arabic

200 gms. H_2O

Start 1 50 PM Temp. 94°C

1st powd. 2 55 PM

Finish 3 0 PM.

Textile World 95, no. 9, 117

Rayon Textile Monthly 23, 609-11, 591-2

Fibres, Fabrics & Cordage 11, 376 (1944)

F. Willcock & H. Kennedy

Proc. Am. Soc. Test. Mat. 44, 6 pg. (1944)

Advancing Fronts in Chemistry I p. 165-180

Concept of textile Fibers Milton Harris

Rayon Textile Monthly 21, 557-8,

609-10,

680-2,

735-5

22 17-18

85-6

147-8

225-6

354-6

455-6

517-18

Superfil
Igelite } also polyvinyl chloride fibers

Act 10$^{\underline{20}}$

running samples

Clean & etching

write up notes

order stuff.

9-27-46

No7 25 g. Diallyl Phthalate
0.25 g. D.P.
2 g. Gum Arabic
200 g. H_2O

Start 3^{15}_{AM} Temp - 95°C
1st Poured 6^{15}
Finish 6^{30} Product — not Polymerized
Thin gummy Fluid

"

No8.
25 g. Diallyl Phthalate
1.5 g. D.P.
2 g. Gum Arabic
200 g. H_2O

Start 4^{25}_{AM} Temp 95°C
1st Poured 5^{15}_{AM}
Finish 5^{30}_{AM}
product — O.K.

"

24

9-26-46

25 g. Diallyl Phthalate
1 g. B.P.
2 g. Gum arabic
200 g. H_2O

Start 4^{30} PM Temp 95° C
1st poured 5^{20} PM
Finish 6^{00} PM

5 Washes H_2O
([illegible])
Dry at 90° C

25 g. Diallyl Phthalate 9-26-46
2 g. B.P.
2 g. Gum arabic
200 g. H_2O

Temp 95° C

Start 9^{00} PM
1st poured - 9^{50} PM
Finish 10^{15} PM

5 Washes H_2O
([illegible])
Dry at 90° C

46

40 g. Diallyl Phthalate
0.8 g. B.P.
1 g. Gum arabic
200 g. H_2O

5 Washes H_2O
([illegible])

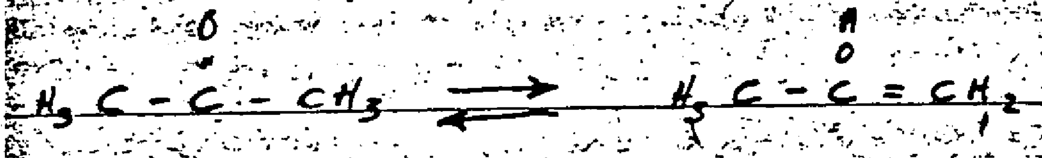
Start 11^{00} am

iallyl Phthalate 2 samples A-B 10-23-46

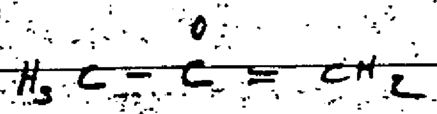
100 gms monomer 1 gm Benzoyl Peroxide	B 100 gms monomer 0.5 gm Benzoyl Peroxide $\frac{3.31}{6}$ (100-50) = 276 mg t BHP
5 Both into 90° bath	
5 Poured A and placed in 90° oven	1:55 poured B and put in 90° oven
remainder in bath d before 1:15	left remainder in bath jelled at 4:00

iallyl Phthalate 2 Samples X & Y 10-24-46

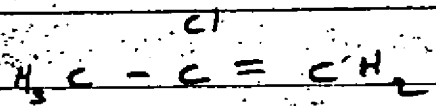
X 50 gms monomer 0.5 gm Benzoyl Peroxide	Y = 50 gms monomer 0.25 gm Benzoyl Peroxide 138 mg t Butyl Hydroperoxide
0 Both into 90°	~~[illegible]~~ bath
Poured & placed in 90° oven	2:15 poured & placed in 90° oven



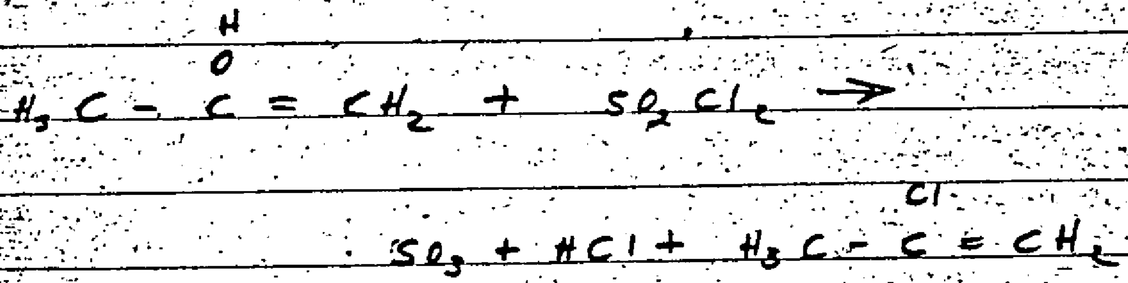
$$H_3C-\overset{O}{C}-CH_3 \rightleftharpoons H_3C-\overset{\overset{H}{O}}{C}=CH_2$$



$$H_3C-\overset{\overset{Na}{O}}{C}=CH_2$$



$$H_3C-\overset{Cl}{C}=CH_2$$



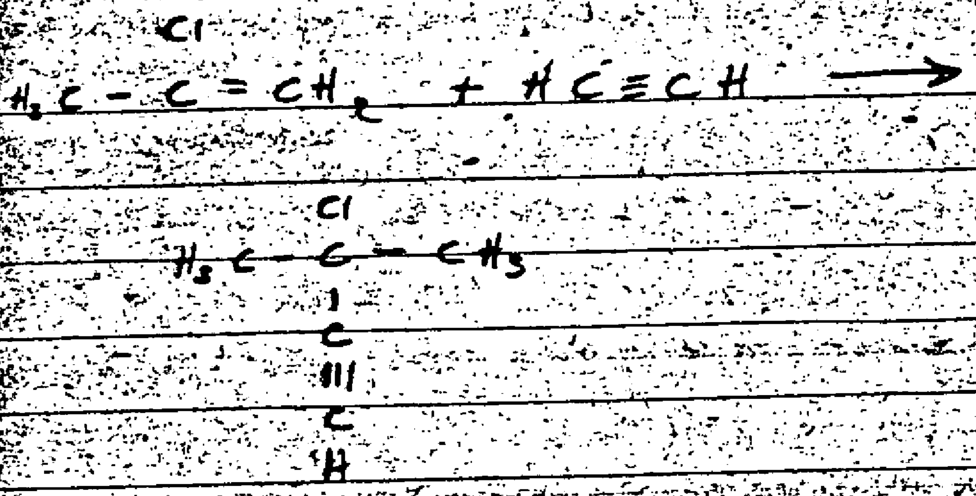
$$H_3C-\overset{\overset{H}{O}}{C}=CH_2 + SO_2Cl_2 \rightarrow SO_3 + HCl + H_3C-\overset{Cl}{C}=CH_2$$

) add @ 0°C 1.1 mole of sulfuryl chloride dropwise to 1 mole of acetone

) after complete addition of sulfuryl chloride, mix for 1 hr. @ 0°C.

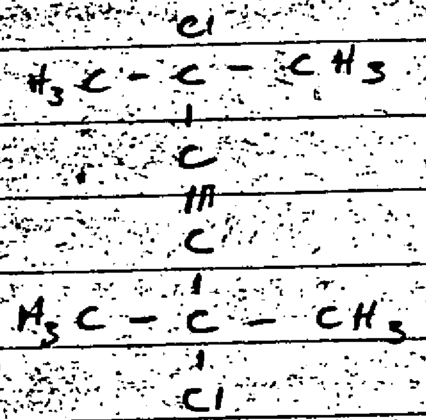
) Then reflux for sufficient time till further ebullition of HCl & SO_3 ceases

) fractionate



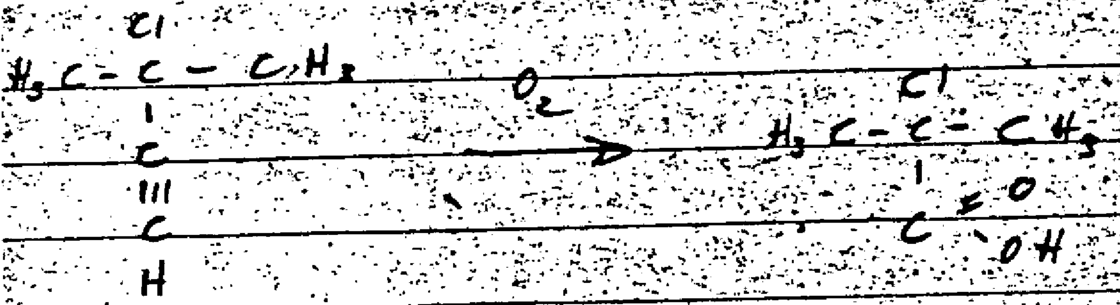
$$H_2C-\overset{Cl}{C}=CH_2 + HC\equiv CH \longrightarrow H_3C-\overset{Cl}{\underset{\underset{\underset{H}{C}}{\overset{|||}{C}}}{C}}-CH_3$$

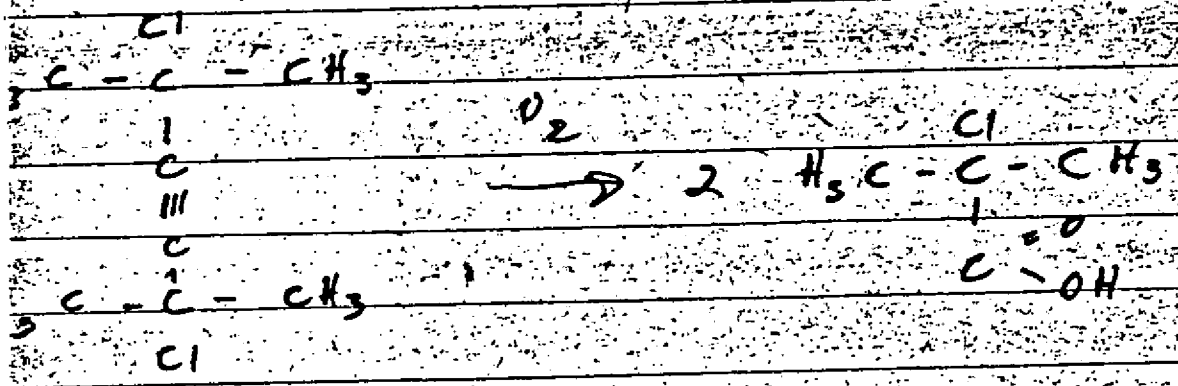
and/or



$$H_3C-\overset{Cl}{C}-CH_3 \\ | \\ C \\ ||| \\ C \\ | \\ H_3C-\underset{Cl}{C}-CH_3$$

) dissolve the propylene chloride in 4 to 5 X vol. of ether (anhydrous)
) purge the system for ½ hr. with CO_2
) pass in acetylene bubbled thru $Cu(NO_3)_2$ into the mixture @ 0°C., passing excess acetylene to acetone absorber for 4 hrs.
) purge system with CO_2 for ½ hr.
) strip off ether under vacuum





disperse both above reactants in 30-40 x wt. of water

) cool to 0°C.

) add 1.1 mols of $KMnO_4$ in the form of a 2% solution @ such a rate as to maintain 0°C. temperature until color appears

) add conc. H_2SO_4 to acidify solution

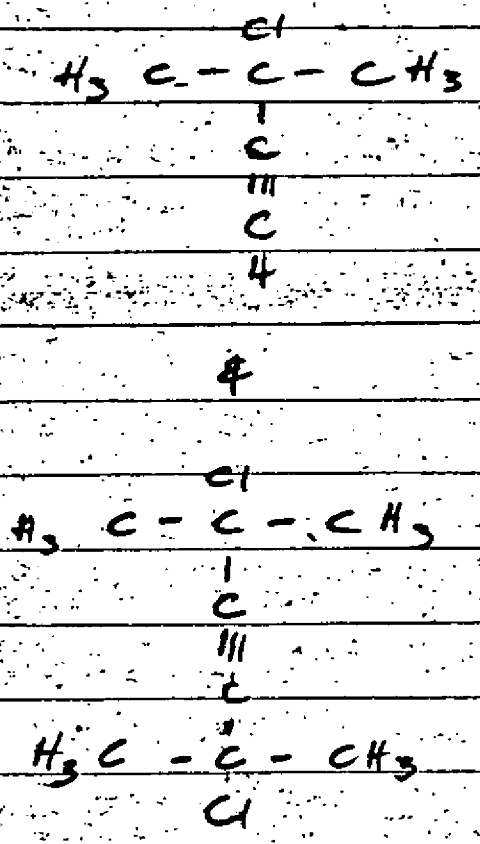
) steam distill until a temperature of 100°C. is attained @ the top of column

) extract the water solution repetitively with equal volume of ether and evaporate off ether in each under high vacuum until we obtain no appreciable return of material

) collect the residue

) get b.p. of propylene chloride

) compute b.p. of

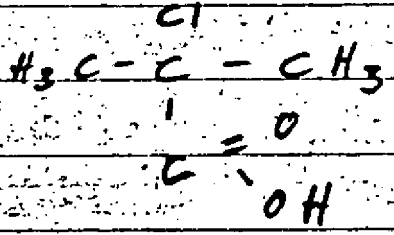


$H_3C-C(Cl)(CH_3)-C\equiv C-H$

$\Downarrow$

$H_3C-C(Cl)(CH_3)-C\equiv C-C(Cl)(CH_3)-CH_3$

) properties & b.p. of



$H_3C-C(Cl)(CH_3)-COOH$

$$\frac{7 \times 18}{141} = 0.89$$

$N_D^{46°}$ 1.4116

Monomer + H_2O $N_D^{46°}$ 1.4117

Wash W N_D^{46} 1.4118

303.5
109.2

194.3 Freon

Total — N-1

1355.4
497.1

857.3 gm Washed Monomer

1024.1 gms monomer
194 gms Freon

= 17.6 %

4-26-61 6b

6/9/61

[illegible] (std) 1.41

[illegible] 1.4417

[illegible] 1.4096

[illegible] 1.5117

Sterling 8-3962

Pre - Polym[illegible]

[illegible]	[illegible]	°C	°C [illegible]
1[illegible]:28	0	30	87
0:33	5	84	89
0:39.	10	85	90
10:43	15	86	88
10:48	20	86	88
10:53	25	85	86
10:58	30	—	—
11:03	35	85	87
11:08	40	85	88
11:13	45	86	88
11:28	P5[illegible]	85	87
11:33	60	86	89
11:38	65	85	88
11:43	70	85	86
11:53	Pour		

Polym[illegible]

Std	Hcl	°C (min)
11:28		82
11:38		82
11:48		83
11:58	—11:53	82
12:08		82
12:13 change to 63 °[illegible]		81
12:43		83
12:53		83

1995 — 2000

69.50

2.61 cu. ft. of air

46 min →

4.05 mg. ozone

independent —

5.3 mg ozone per hr

Mr. Kroto

38-04 - 48 LIC

ST 4-6400

AC-DC appliance

324 W. 42 nd

crystal

ME3-0388

$6 - per month

$23.50

gms monomer / 200 HOH

~~2 gms BP.~~

TBPC - 2%

30% BP

70% t-HPP

Dispersing agents (ARMAK)

~~[illegible]~~ 0.5 g / 100 cc HOH

↓ if powder

0.2 g / 100 cc

↓ if powder

0.1 g / 100 cc

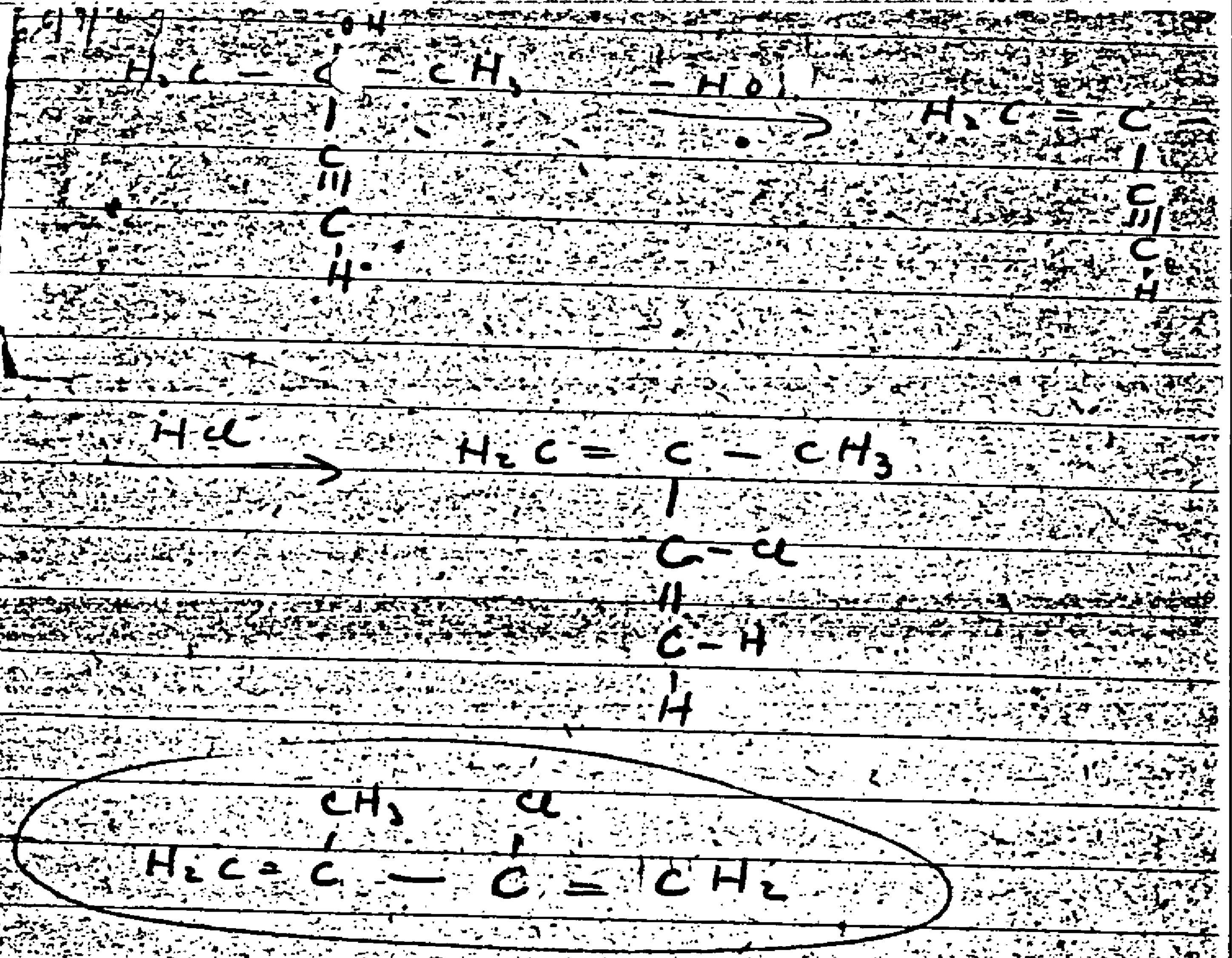
use 7 l flask
with Hirschberg stirrer

80° bath

3.31
35
1650
993
115.85
6) 115.85
19.31

150 mg BP

$\frac{3.31}{6}(500-150)$



Methyl chloroprene CA 35, 588

V.N. L'vov - Akopyan Polymeriza
J. Gen Chem U.S.S.R. Vol. 11, p. 297-314

Air Reduction Sales
Linde Air Prod.
Shawinigan

4.00 6.00 8.00
Jan 15.

A. Brothman & Assoc.
1.50

N.Y. Office
Hillside, N.J.
Pioneer Oil Transport,
305 Long Ave.
Hillside –
opp. Pulaski skyway

14 screen mesh no dust
almost like sand
not dust –

14 no dust
if powder mat –
25 lbs @ 1.50 for entire

Hillside, N.J.

out early in morning, again in afternoon
Friday – call ~~tomorrow~~ afternoon
Mr. Small ext. 195 – MU 2-6700

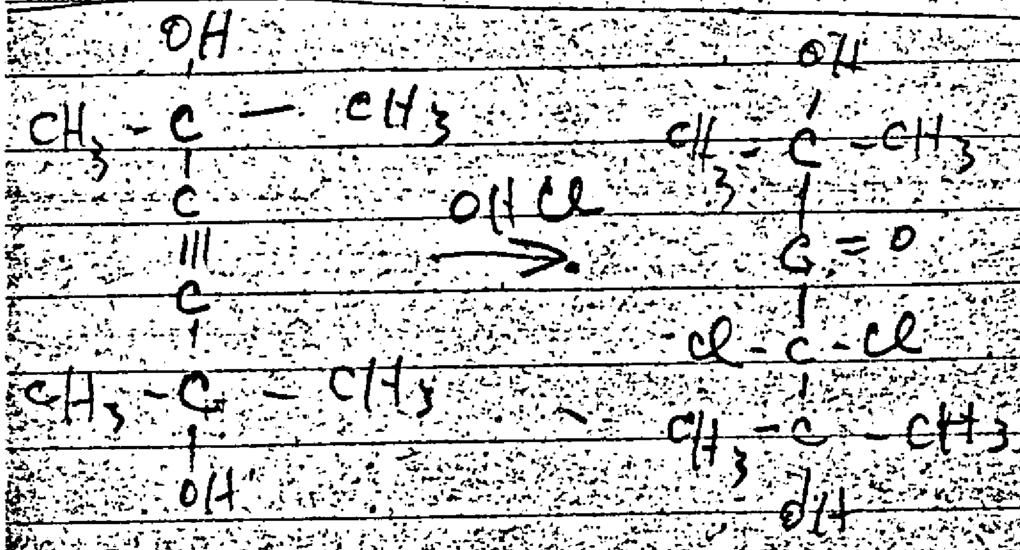
10 of 50 Philadelphia

CA 30 8241 (36)

Chemistry of Acetylene — p. 773

① formation of acid + CO_2 — Compt. Rend. 152, 1603b (1911)
② ozone — JACS 58 2272-3 (1936)
③ dilute $KMnO_4$
JACS - 45 - 795-9 (1923)
① above
cf. Compt. Rendus 149, 381-3 (1909); 150 (1523-5) (191
Ann. Chim. Phys. 30 329-35 (1913) ← Dupont
also chromic acid, HNO_3, peracetic, ozone

on Kazarian's method:
Zaklaova - Sci Reports Leningrad State Univ.
2 #2 (162-95) (1936) C.A. 32, 2506 (1938)

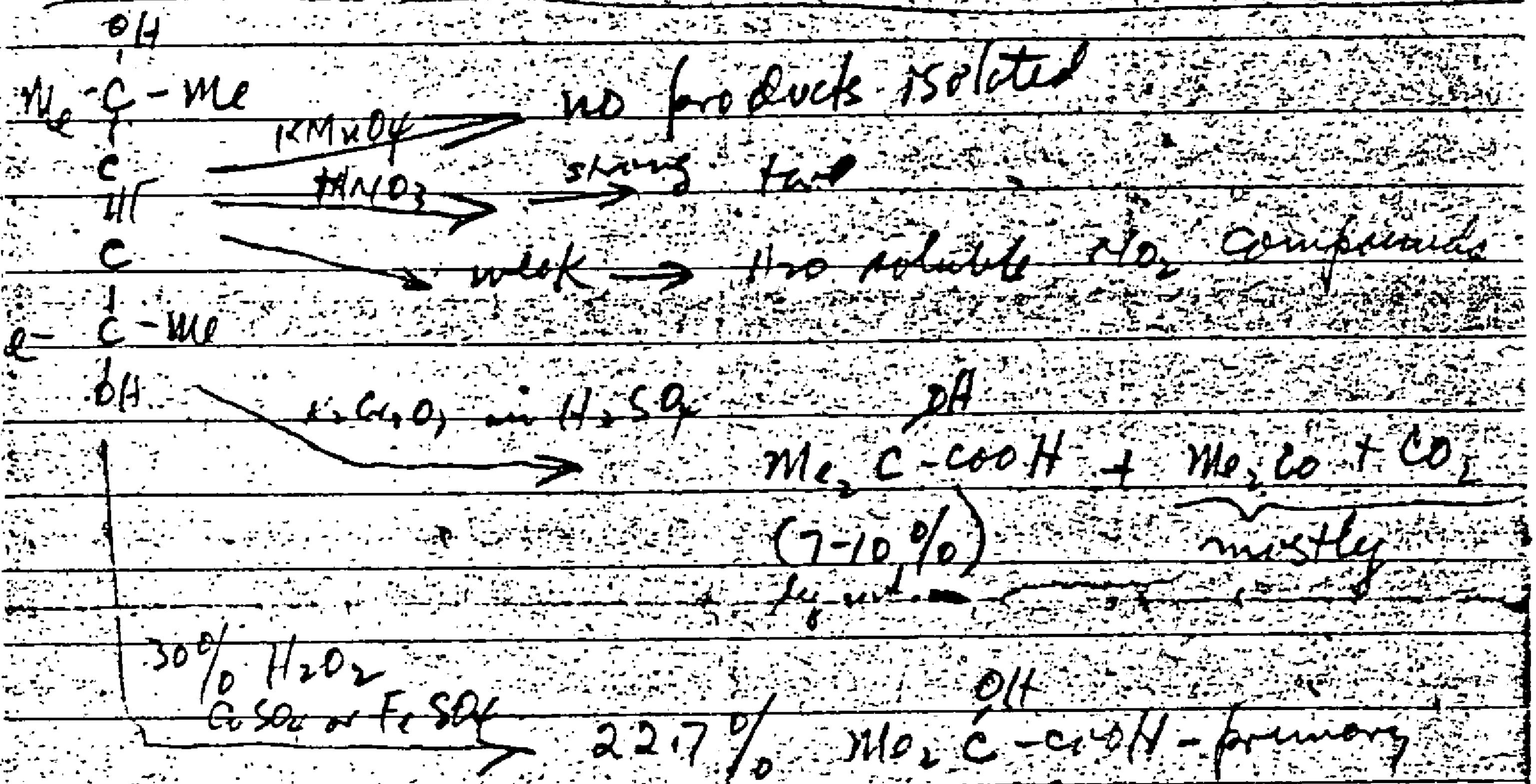


(CA - 35, 3227 (41))

C.A. 35, 5850 (1941)

V. N. L'vov, Akopjan, Polyuta

J. Gen. Chem. (v. 35 R) 11 (298-304) (1941)



$Me_2C(OH)-C\equiv C-C(OH)Me_2$

$\xrightarrow{KMnO_4}$ no products isolated

$\xrightarrow{HNO_3}$ strong → tar

weak → H_2O soluble NO_2 compounds

$\xrightarrow{K_2Cr_2O_7 \text{ in } H_2SO_4}$ $Me_2C(OH)-COOH$ + $Me_2CO + CO_2$

(7-10%) mostly

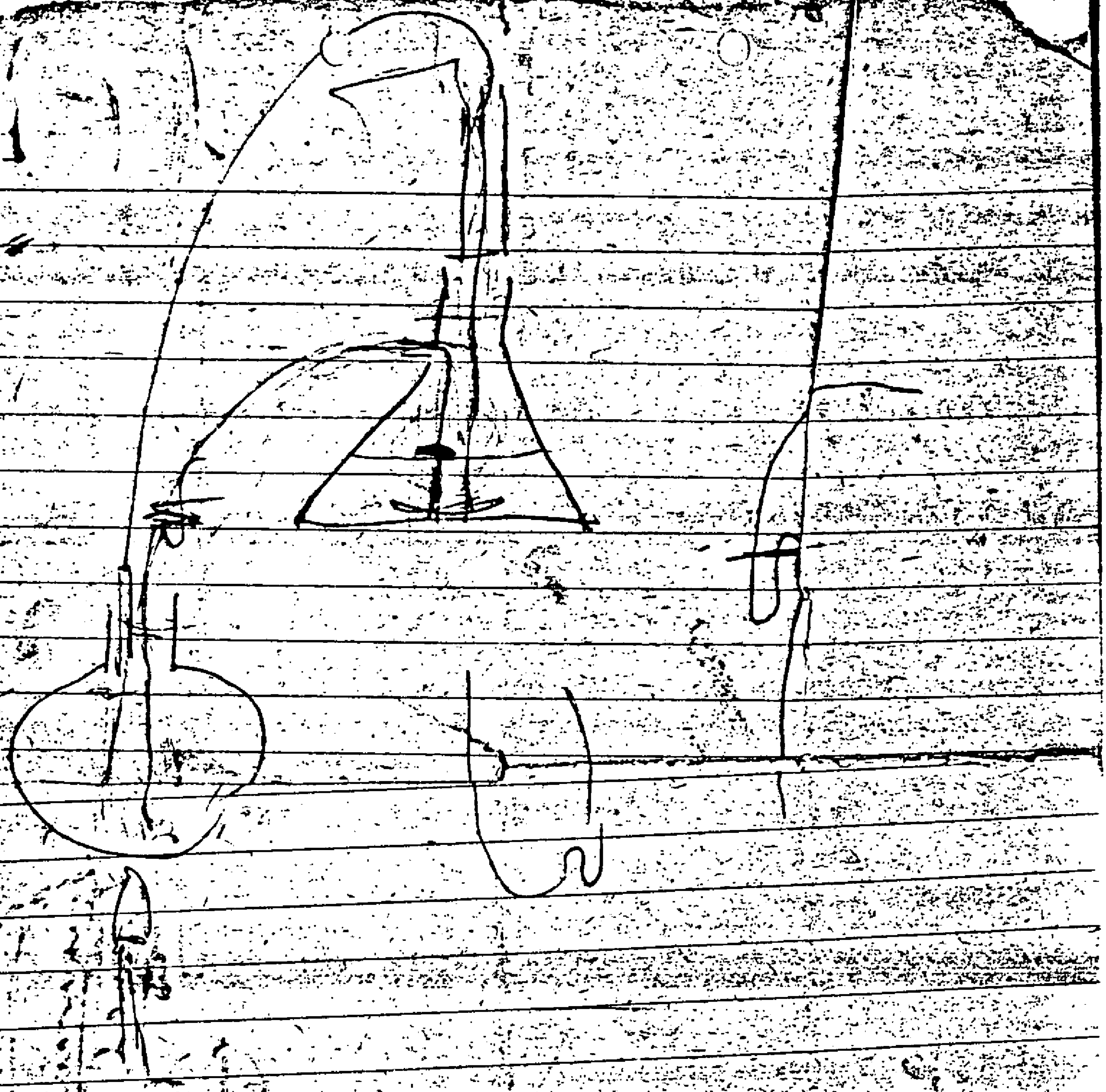
+ [illegible]

$\xrightarrow[CuSO_4 \text{ or } FeSO_4]{30\% \ H_2O_2}$ 22.7% $Me_2C(OH)-COOH$ - primary product, but partially oxidized further to CO_2 + Me_2CO → HCOOH + OHAc

Schwartz, Frank

235 Hart St.

6/2/50



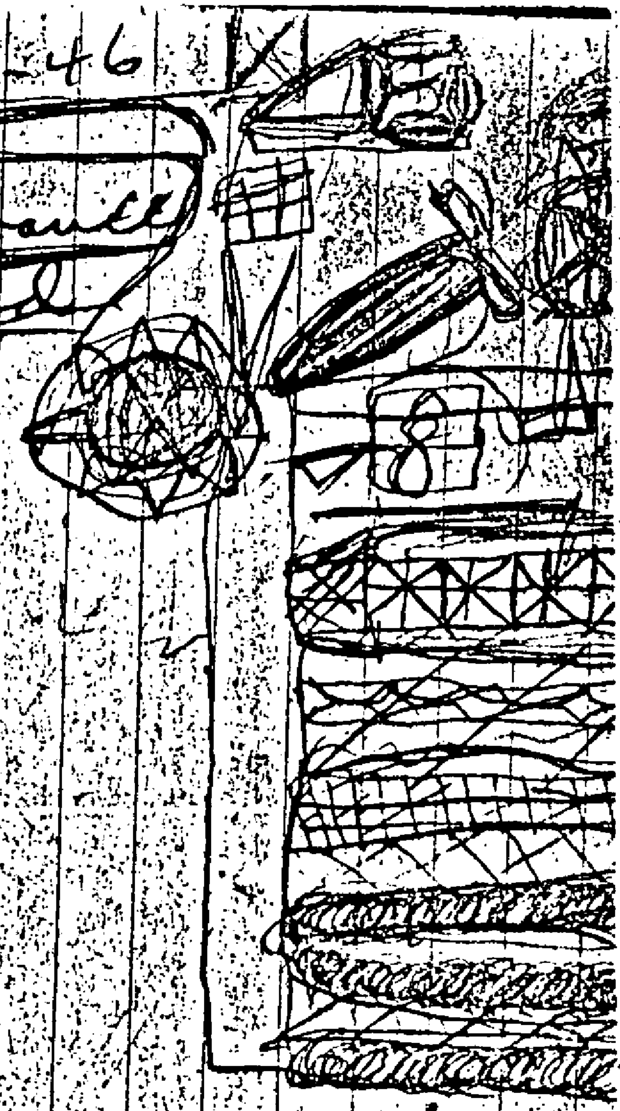
U6150
277

10-28-46

① insurance

covered

②



Zehlasson
mitte
Re.

Lab. Organization

1. Set Rept Books
2. Set Bi-Weekly Repts started (M6)
   (one for end of this week)
3. Clean Place – throw out junk [illegible]
4. Organize Files
5. Organize Inventory List
6. Set [illegible]
7. See abt Drums
8. See abt other storage.
9. See abt Rhodamine for Eddie
10. Fix outline

Lab Work

1. MeMe Molding Powder
   - a. Try [illegible]
   - b. Try [illegible]
   - c. Try Synthetic Waxes
   - d. Try agar
2. MeMe Powder mol wt Detn.
3. MeMe Sheet – o. a. f. a.
4. Polystyrene Sheet
5. Check alkyd resin work
6. MeMe – $AlCl_3$ Runs.

① Frank [illegible] 6-11-46

[illegible]

-5151

[illegible]

② Frank - [illegible]

[illegible]

317.8

[illegible]

③ [illegible]

524.8

[illegible]

Monomer Portions

970
214
756

#1 1378.2 Total
1177.5
200.7 ≈ 214 cc

#2
1177.5
969.5
208.0 ≈ 222 cc

756
222
534

#3
969.5
740.3
229.2 ≈ 245 cc

534
245
289

637.9

Washed Monomer Quantity
876.3
288.1 Tare (Mixing Flask)
588.7 gms washed Monomer

4

[illegible] [illegible]

[illegible] [illegible]

456.0
77.8 Tare
2

M[illegible] [illegible]

621.2
135.1 Tare
486.1

F[illegible] Paper 3.1
1.3 gms
1.8
[illegible] 3.2 6
0.6
4.4

0.9
1.6
0.7 mg
5.1
8.1
[illegible]
0.4

Flask [illegible]
303.4
- 83.1
[illegible] ⟶
5.8

84 = 1.42
[illegible]

Monomer Portions ①
(NAOH + H_2O)

6-12-46
244 Gms
Empty flask
+ cotton

No 1.

1861.5 Gms
1651.0 "
210.5 Gms ≈ 224.7 cc (225 cc)

No 2

1651.0
1394.0
257.0

265
+237
502

No. 3

1394.0
1169.3
224.7 ≈ 241 cc

25.8
241
267

No. 4

1169.3
924.2
245.1 ≈ 262 cc

No. 5

924.2
629.3
294.9 ≈ 310 cc

③ 6-20-46

Total Wt

1598.5

524.8 Tare 23

1073.7 gm = 1180 cc.

$\frac{1073.7}{100} \times 20 = 215.74$ mg.

B.P.

$\frac{1073.7}{100} \times 99.3 = 1.066$ gm.

T.B.H.P.

B.P.

0.2169

tare 0.0006

0.2163

T.B.H.P.

1.0665

0.0027

1.069 gm

② 6-12-46

Air polym.

Time	min	t°	Rate
1:25	0	30	73
1:30	5	63	75
1:35	10	84	91
1:40	15	76	83
1:45	20	82	81
1:50	25	85	82
1:55	30	84	90
2:00	35	85	84
2:05	40	85	81
2:10	45	85	83
2:15	50	85	82
2:20	55	85	78
2:25	Air added [illegible]		
2:30	65	59	43
2:35	70	45	2
2:40	75	40	1
2:45	80	32	1
2:50	85	26	1
2:55	90	22	1

4^{00} 5^{00} — 7°-8°

4^{01} . hydrolysis of 1st frac.

246 gms. product
135 cc. H_2O
considerable gas evolution —
acetylene coming off

($10cc\ H_2O$
lost)

5^{00} #2 withdrawal

$$\begin{array}{r} 223 \\ \underline{553} \\ 776 \end{array}$$

553 gm. product ($270cc\ H_2O$).

12-5-77

Withdrawal #3 $6\frac{00}{PM}$

Tare 262
553 grams + 303 H_2O
815 Tot!

Withdrawal #4 $8\frac{00}{PM}$

Tare 243
553 + 303 H_2O
796

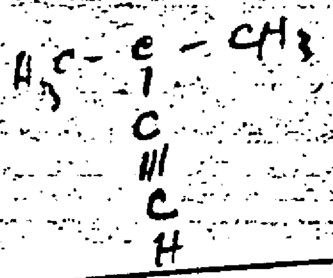
Withdrawal #5 Final

Found ☒ 1512 (1512)

12-16-46

DEC 16 1946

Quantities



$H_3C-C-CH_3$, $C \equiv CH$

CaC_2 - $\frac{64}{.8}$ = 80×2 = 160
×.85
136 gms.

tare-793
136
929.1

KOH

$\frac{56}{\cancel{0.85}} \times 2 \times \cancel{0.85}$ = 112 gms.

tare - 929.2
112.0
1041.2

acetone

~~58 × 2 × 0.85~~ = 98 gms

116
0.85
580
928
98.60
0.8
= 120 mls.

~~168~~
~~98~~
~~266~~

154.5
98.0
252.5

ether

300
0.85
255~~00~~ gms.
0.83

= 308 mls.

1044.8 – fuel
255.0
1296.8

A

(12 - 23 - 46)

11^{00}

pH. of Solutions :-

	ether	water layer
C - 24	6.8	~~6.8~~ 6.6 after stirring
C - 23	8.2 neutralized to 6.5	6.4

distillation of C-23 - ether solution

2^{05} - distillate - flask start

2^{10} - 35° - 43°

2^{20} - pH is 6.7 - about 50 mls. ether taken over. This used to wash residue in original beaker and filter paper and returned to still pot

2^{40} - resume distillation

dist. flask C-23

2^{47} - 37° 65°

2^{57} - 38° 55°

3^{05} - about 125 mls. ether taken off - pH - 7.1
1 drop conc. HCl - 4.5
few mgs K_2CO_3 - 7.35 (powdered)
4 drops 10:1 HCl - 6.75

3^{37} - resume heating

3^{50} - 37 (61)

4^{00} - 25 mls. more ether off
pH - 6.7
resume heating

4^{25} - 41.5 90 - slow distillation.

4^{35} - 41. - 92.5 - no ether coming over - lower bath; stop heating

4^{53} - $\boxed{6.72}$

G-23

5^{03} - resume heating with wax bath

5^{15} - distillate flask bath - chart
60 112 140

10 mls of distillate have come over - colorless - no ether odor - slight odor of H_2S or something similar

5^{20} 83, 125 162.5 -
column 74° - temp. of distillate rising all the time - considerable reflux up the column -
- cut flame -

5^{24} - 86° - 130 - 164 -

Note - 2 phase system appears at head of condenser

$pH = 6.0$

12-24-46

11^{10} - start heating

11^{24} 125 144 - reflux begins up column - jacket temp. 76°

C-23

11^{30} - no distillate, tho reflux taking place to small extent -

distillate	flask	bath
(76°)	141	162

Jacket - 96° -

stop distillation (possible decomposition ?) - cool - pH = 6.3

---

total distillate - 2nd fraction

58.8
53.4
5.4 gms.

1st fraction - mostly ether.

172
te - 77.9
94.1 gms

filter crystals + recrystallize
from hot CCl_4 –

Note – after distillation, the residue consisted of a mass of yellow-brown crystals plus about 10-15 mls. of a thick liquid –

this was filtered, the crystals recrystallized – however some crystals remaining in flask, were dissolved in hot CCl_4 + also recrystallized –

The liquid part of the residue was mixed with some of the CCl_4 –

Yield – 12 gms. – recrystallized

about 2 more gms. in
mother liquor

12-26-46 C-24

c-24 - ether distillation

$11^{\underline{00}}$ - pH = about 8.6 (after filtration)

add 6 drops 10:1 HCl - 7.93

add 6 " " " - 4.8 - 5.8

rose during pH reading

ether solution became cloudy because of dispersed dilute HCl solution

add 2 more drops — 2.6

adjust to about ← 6.45

$2^{\underline{05}}$ - start distilling over ether

dist.	flask	bath
35	45	66

$2^{\underline{20}}$ - about 50 mls. ether off - pH = 6.45

$2^{\underline{25}}$ - resume distillation, add balance of distilland -

$2^{\underline{37}}$ - 36 54 73

$2^{\underline{45}}$ - about 100 mls. off - pH - 7.0
adjusted to " 6.5

2^{52} – resume heating

C-24

2^{58} – dist. flask bath

35 78 85° – coming over slowly

3^{10} – 31 91 95 –

the distillation has almost stopped

3^{24} 36 92 95 –

Jacket temp. to 57 to aid

very little ether coming over –

residue is about 75-80 mls.

3^{38} – stop heating with water.

3^{56} – start heating with bath wax

4^{05} – 77 107 154 Jacket 79 –

temp. rising steadily

4^{11} – 93 127 182 78 –

about 20 mls. of distillate have come over – light yellow color – stop for pH determination

4^{25} pH = 7 – adjust to 6.4 –

C-24)

mass of crude hexyne -

18-20 gms.

6/6/50

C-24

Note: on ~~basic~~ acid side, an oil separates ~~[illegible]~~ about 2 - disappears on basic side

12-27-46

pH - 6.8

11^{15} - start heating & resume distillation

	dist.	flask	bath	jacket
11^{18} -	98°	108	151	98°

cut jacket temp. - oil & H_2O coming over

11^{38} -	98°	110	158	90

dist. rate holding steady - stop for pH determination - about 20 mls. out

Note - sample consists of heavy oily layer resting on about 1/2 its volume of water

pH = 7.5

C-24	dist	flask	bath	jacket
2^{58}	90	179	185	180

small quantity of dist. coming over - dist. temp. no indication of b.p. for too little is coming over to raise thermometer temp. - boiling in flask, but no crystal formation - raise temp. to increase rate

Note - seems probable that at this stage a small amount of mesityl oxide is coming over - (handbook b.p. 128°-131°)

3^{12} stop distillation

dist.	flask	bath	jacket
87	195	210	105

cool to prevent possible decomposition -

Note - product has sharp, sweet odor ①

② flask has heavy residue of about 25-30 mls. 6-6-50

12^{17} - adjusted to 6.38 C-24

1^{15} - resume heating

1^{20} - stop to separate water layer - pH of water layer 6.8 - volume, about 5-8 mls. change receiver

2^{00} - resume heating

2^{25} -

dist	flask	bath	jacket
100°	120	180	86°

2^{35} - distillation of 100° fraction has stopped - combine this with 2^{nd} fraction - cut

2^{40} - increase heating

2^{47} -

dist.	flask	bath	jacket
96°	163	197	103

reduce heat - small amount of last fraction coming over 6/6/50

12-26-46

pH of C-26

water layer	ether layer
8.7	about 1.35
{adjust to 6.9} {keeps going up}	adjusted to 6.8

12-27-46

7.18

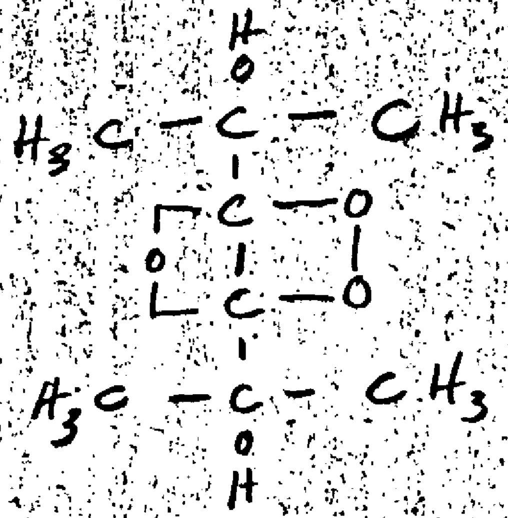
adjust to 6.82

#1 [illegible]

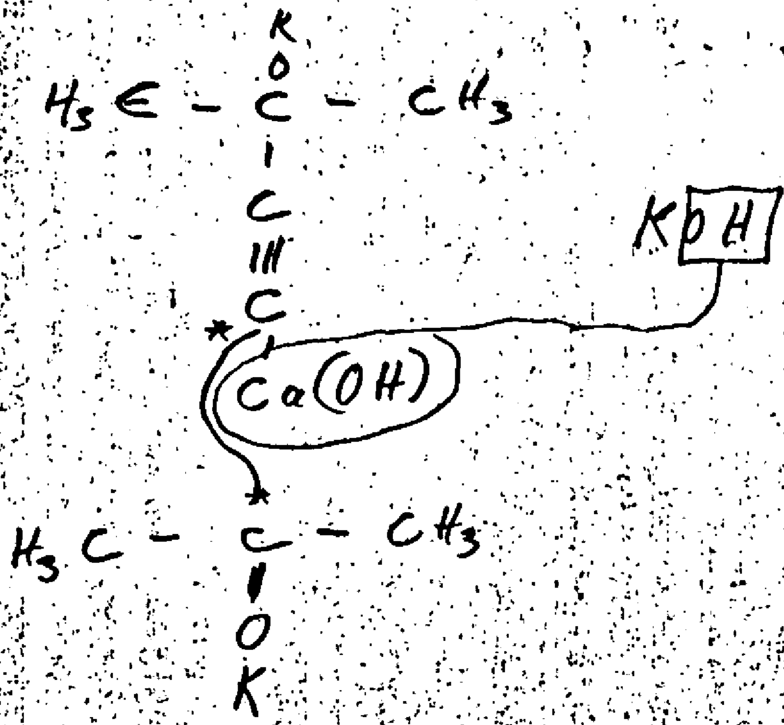
100 —— 14-0 53

75 —— 14-0 49

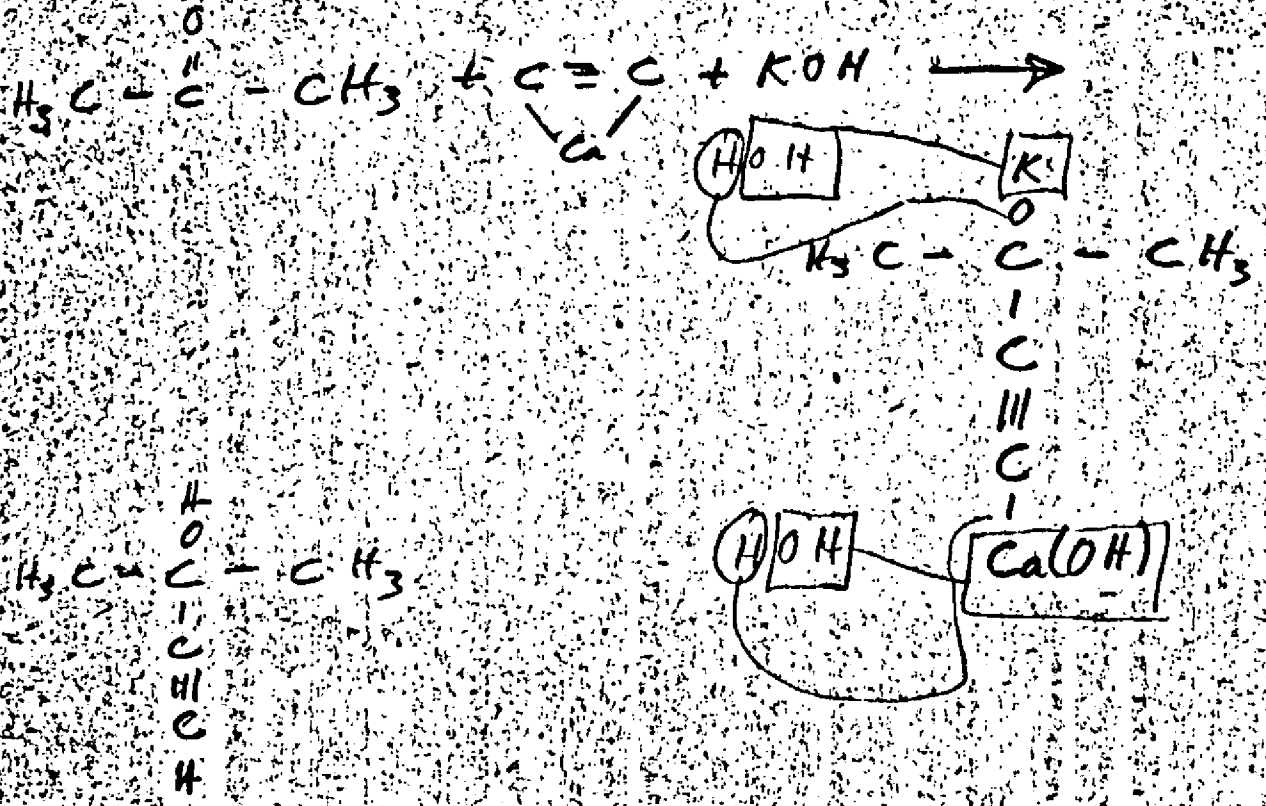
to [illegible]



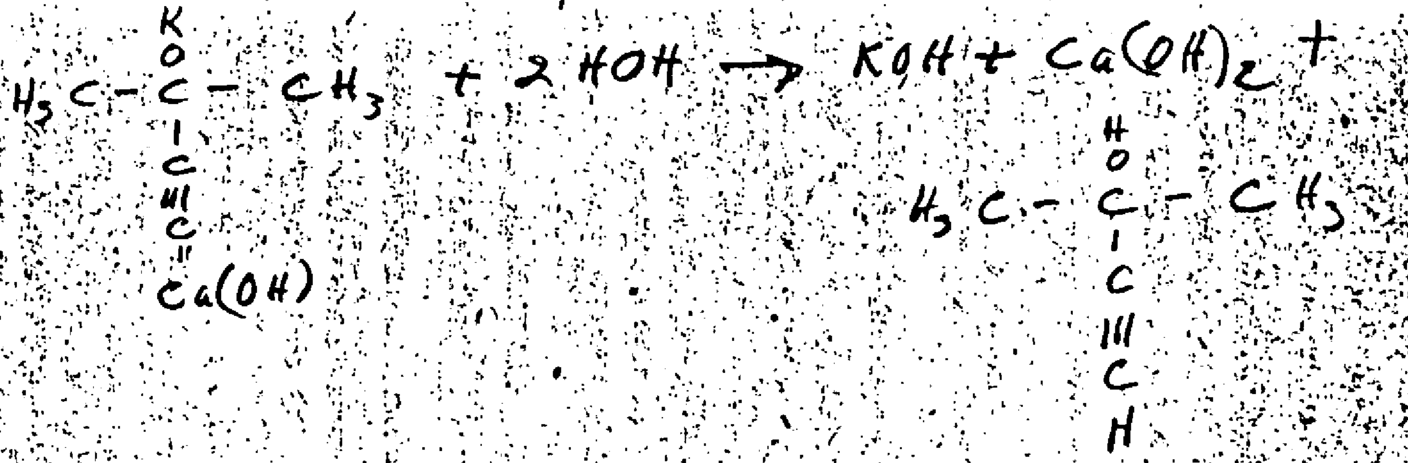
6/6/50



$Ca(OH)_2$



O
H3C – C – CH3 + C ≡ C + KOH →
Ca
H OH
K
O
H3C – C – CH3
C
C
H OH
Ca(OH)
H
O
H3C – C – CH3
C
C
H



$$H_3C-\overset{\overset{K}{O}}{\underset{\underset{\underset{\underset{Ca(OH)}{\|}}{C}}{\|\!|}}{\underset{C}{|}}}{C}-CH_3 + 2\,HOH \rightarrow KOH + Ca(OH)_2 + H_3C-\overset{\overset{H}{O}}{\underset{\underset{\underset{\underset{H}{C}}{\|\!|}}{C}}{|}}{C}-CH_3$$

awe
5/9/7

carbide acetone butyne

$A + B \longrightarrow C$

butyne acetone isoprene

$C + B \longrightarrow D$

$$-\frac{dA}{dt} = \boxed{k_1} AB$$

$$-\frac{dC}{dt} = \boxed{k_2} CB - k_1 AB$$

$$\frac{dD}{dt} = k_2 CB$$

1204.1

~~1172.50~~
~~1083.69~~
~~88810~~
~~77726~~
~~11084~~
~~45280~~
~~36173~~
~~91070~~

~~.983~~

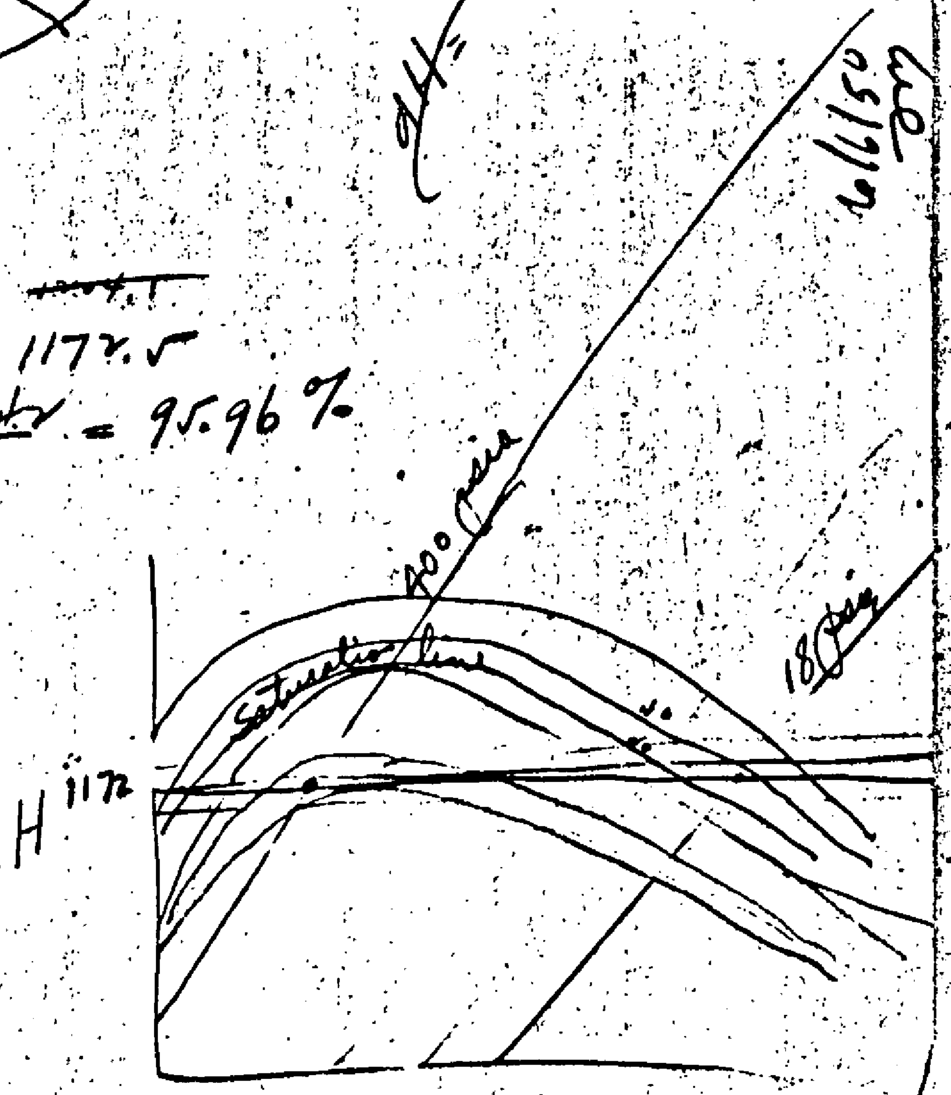
→ h_f

~~1204.1~~

$$424.2 + x\,779.8 = 1172.5$$

$$X = \frac{1172.5 - 424.2}{779.8} = 95.96\%$$

$dH = C_p$



8:30 Bath at +10°C sufficient to keep temp of mix at 14°C.

855 Started cooling

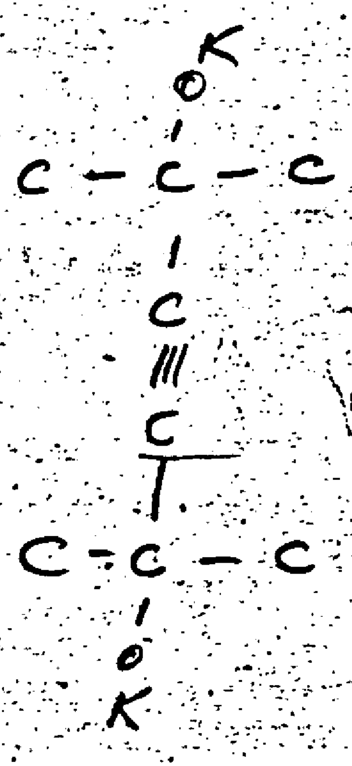
920 Started adding ice

926 Finished adding. Temp of bath 12°C
Temp of mixture fell from 0°C to -2°C.
Bath removed.

6:15

~~KOH~~ CaC_2 & coke

1) Absorber
2) Kazarian × Today's run
3) Binder



KOH ratio ✓

reaction time ✓✓

temp. of acetylene absorption ½ ✓

reaction temp?

Sp. Gr

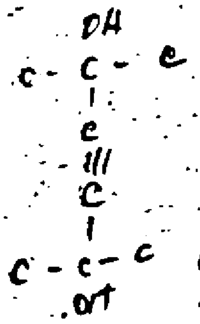
91% 1.821

75% ✓

50% ✓

25% ✓

10%



95% 1.840

100 g = 0.95

100 g = 0.90

$\frac{0.91}{0.95} \times 100 =$

$\frac{0.75}{0.95} \times 100$

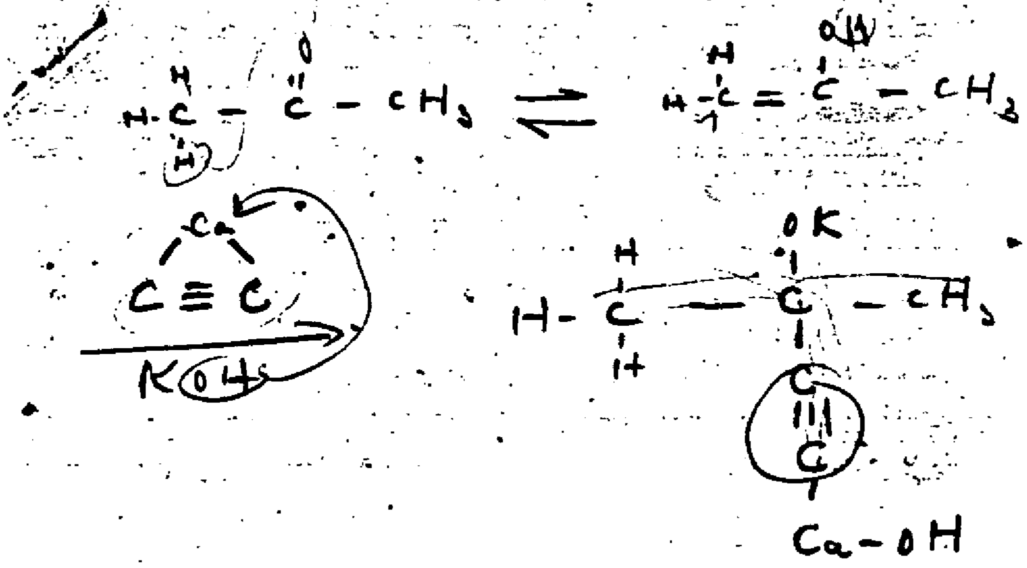
NOV 27 1946

C O

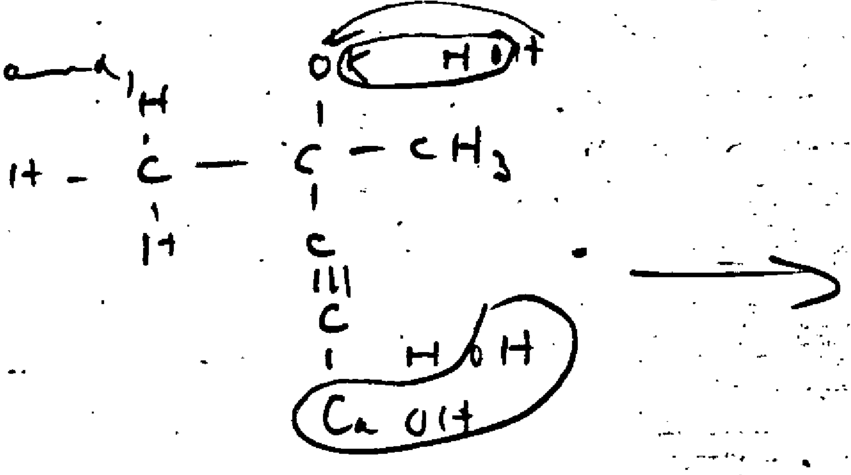
297 gms KOH

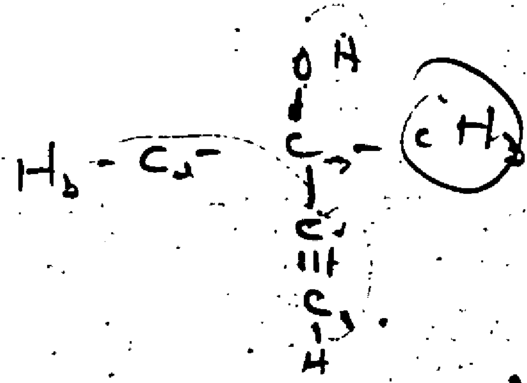
360 gms. CaC_2

600 gms. ether



Butine





3-Methyl-3 Hydroxy-Butine-1

$\boxed{12-9-46}$

Butinol

Quantities

KOH — $\frac{56}{.85} \times 2$ — $\boxed{132 \text{ gms}}$

CaC_2 — $\frac{64}{0.8} \times 2$ — 160
16 — 10% excess
$\boxed{176}$

acetone — 400 × 2 — $\frac{800 \text{ gms}}{0.79}$ = 1015 mls.

---

use 15% less than above —

KOH — 112 gms.
CaC_2 — $\boxed{150}$ "
acetone — $\boxed{680}$ " = 860 mls.
total vol. — about 947 mls.

acetone - 802.3

680

$\boxed{1482.3}$

CaC_2

1482.7

150

$\boxed{1632.7}$

KoH

92.8

112.

$\boxed{204.8}$

12-11-46

Time	Min.	Flask	Bath	Notes
2^{42}	0	30	30	start
2^{47}	5	33.5		
2^{50}	8	35	30	
2^{52}	10	36	29	
2^{57}	15	34	26	– add KOH
3^{00}	18	35	26	– becoming viscous
3^{05}	23	36	27	
3^{07}	16	39		– need setting
3^{12}	21	48	4	– strong heat of reaction
3^{18}				– remove motor – no stirring stir by hand
3^{22}	–	40	– 4°	add 100 ~~mls.~~ gms.
3^{24}	–	33°	– 40	acetone
3^{26}	44	44	–	
3^{32}	50	41	– 4	– thick sludge
3^{34}				add 250 mls. acetone

min Flask Bath
3:40 - 58 35 6 added KOH

3$^{\underline{46}}$ - 64 34 4

3$^{\underline{55}}$ - stop stirring -
heavy sludge clay color
mixed with red color

4:15 - 35°C
17 temp rose to 37; put in cooling bath
20 41° in ice bath
30 44°C " "
40 45
45 49 " "

[illegible]

Vapor temp °C	Fraction
56 - 85	[illegible]
85 - 90	[illegible]
90 - 95	
95 - 105	31 ml
105 -	

12-10-46

Solubility of acetone in various Solvents - adding solvent to +2 mls of acetone

solvent	Results
① $CHCl_3$	1:1 - completely miscible
② CCl_4	1:1 - completely miscible
③ $Cl_2C=CCl_2$ tetrachloro-ethylene	1:1 - completely miscible
4) trichloro-ethane $ClCH_2-CCl_2H$	1:1 - completely miscible
⑤ acetylene tetrachloride	1:1 - completely miscible
⑥ ϕCl	1:1 - completely miscible

12-10-46

Butine synthesis

Quantities } 85% of 2 mols for KOH, CaC_2

KOH - 112 gms.
CaC_2 - 136 gms.
acetone - 680 gms. (about 860ml

acetone
tare - 803.8
680
1483.8

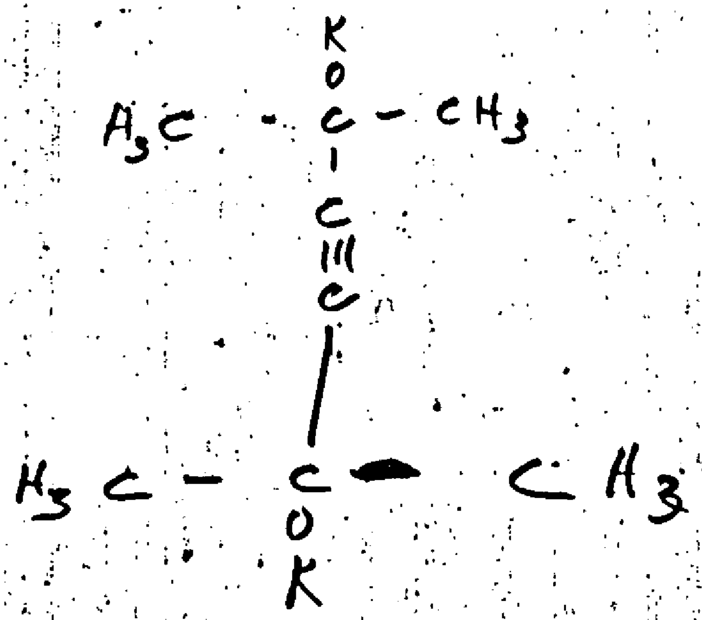
KOH
tare - 93.1
112.
205.1

CaC_2
205.4
136
341.4

we 5/7/77

$CH_3COCH_3 +$

$+ H_2O$



12-17-46

Quantities

CaC_2 $\frac{64}{0.80} \times 0.85 \times 2 = \boxed{136 \text{ gms.}}$

KOH

$\frac{56}{\cancel{0.85}} \times \cancel{0.85} \times 2 = \boxed{112 \text{ gms.}}$

acetone

12 - 18 - 46

Starts coming over at $2^{\underline{40}}$

46° - 98 mm.

---

rose from 28° - 47° in about 4 minutes

---

remove flame : $2^{\underline{43}}$

down to 42° - bath 79°

vapor flow cut down

$2^{\underline{50}}$ - holds at 44° - $^{45°}$ steady

distillation rate - slow -

2 phase system in upper portion of condenser

$3^{\underline{00}}$ - flask - 91°; no more distillate at 100 mm, tho boiling -

$1^{\underline{st}}$ fraction about 15-20 mls. either water or mix of butanol + H_2O

---

next fraction

3^{35}. - start heating
bath - 115°, flask 76°
column 56°, 50 mm.

NOTE: !!!! - crystals on surface of flask - HEXINE

additional 10 mls. over from 1st fraction - probably water + H_2O-butine mix

---

4^{30} - replace with heated condenser + start vacuum at 100 mm.

5^{20} - vacuum - 3-4 mm.
distillate - 68° ; bath 185°
flask. 182° ; column 115°
condenser > 150°.

C-21 - distillation

— ether-acetone taken off initially under atmospheric pressure —

— then additional portion under vacuum 50-100 mm. at about 29-31° - end of this fraction -

---

check pH - 5.2, after adding small portion of Na_2CO_3, it went up to 5.9, tho all salt didn't dissolve

— at 6.3, remove to 500 mls. flask, so as to maintain pH

Distill

3^{55} - distillate 40°, about 150 mm. flask 61° no heating because of initial bump of column - very slow distillate.

4^{03} - distillate 42° - 100 mm. flask - 54° - steady rate

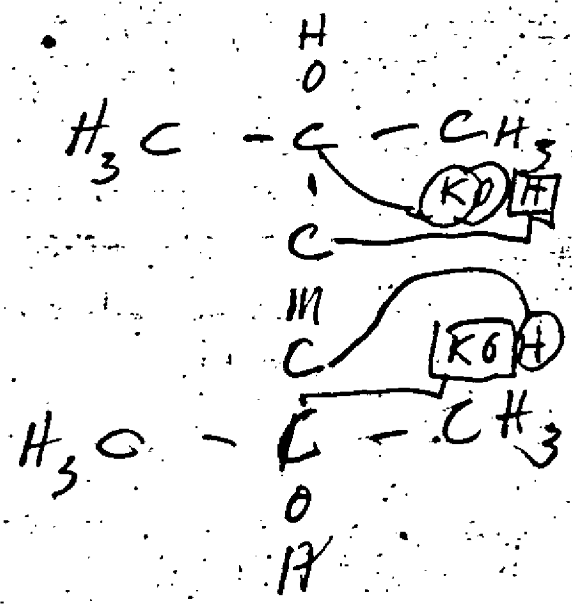
4^{05} – starts heating to increase rate of distillation

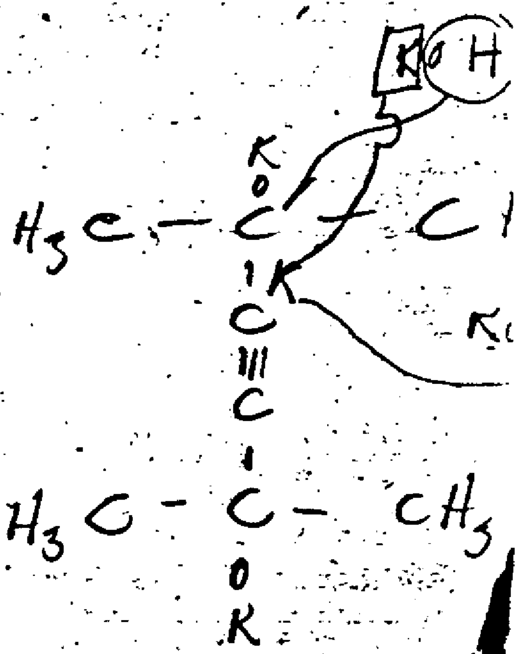
4^{15} – 91 mm., distillate 45°, flask 61°, bath 113° – apparently water + another phase coming over – water made in excess

Note

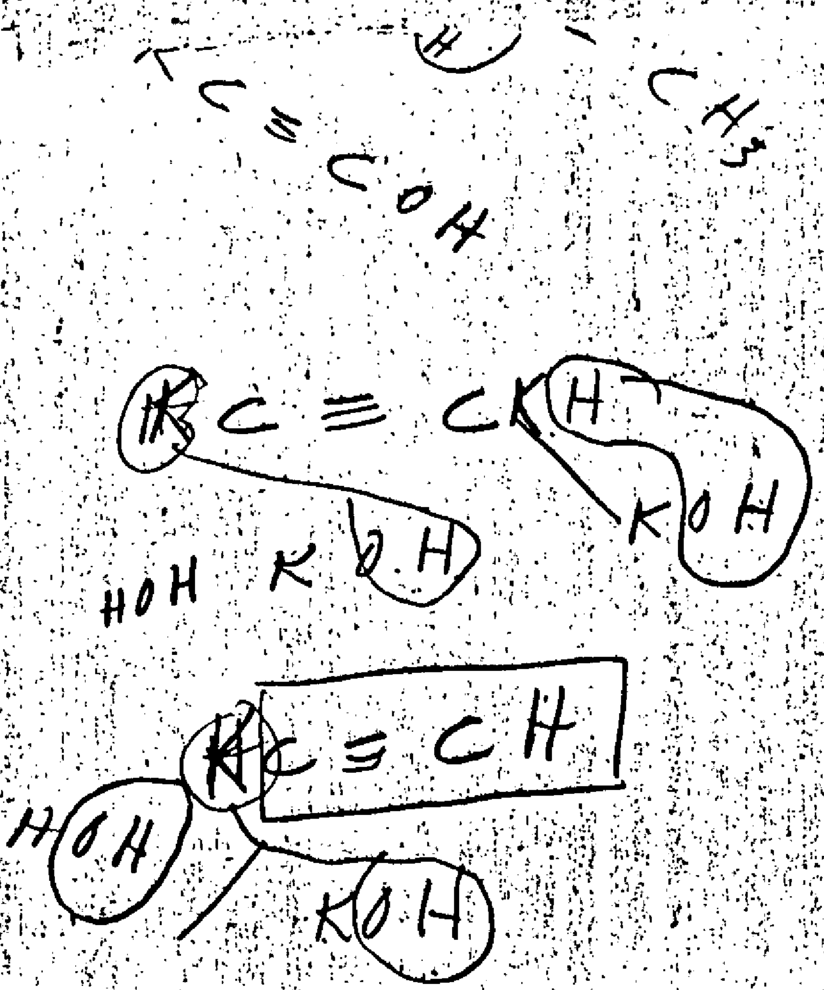
4^{25} – boiling steadily after wooden applicator sticks placed in flask – previous temp. incorrect due to unsteady state of vapor – no bumping now – 49°, 98 mm handbook – for H_2O – 51°, 100 mm. – flask 70°, bath 43°

4^{40} – distillate about 46° – 100 mm temp. drop due slowing up of distillation



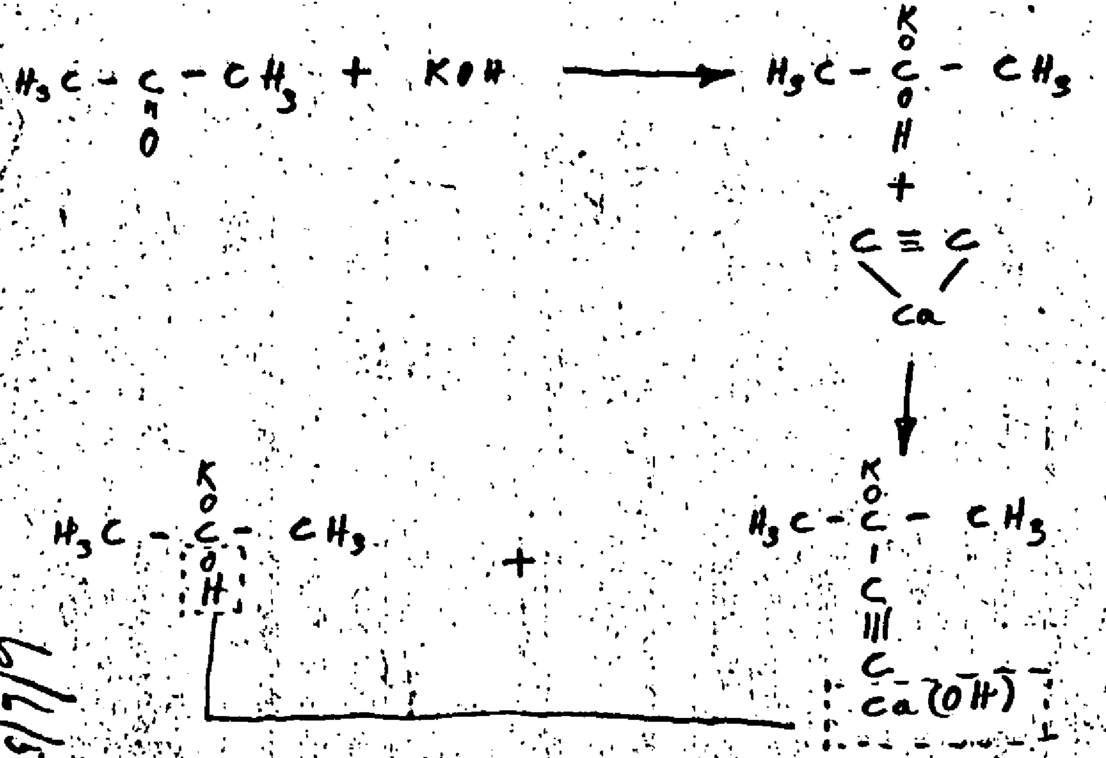


6/6/50



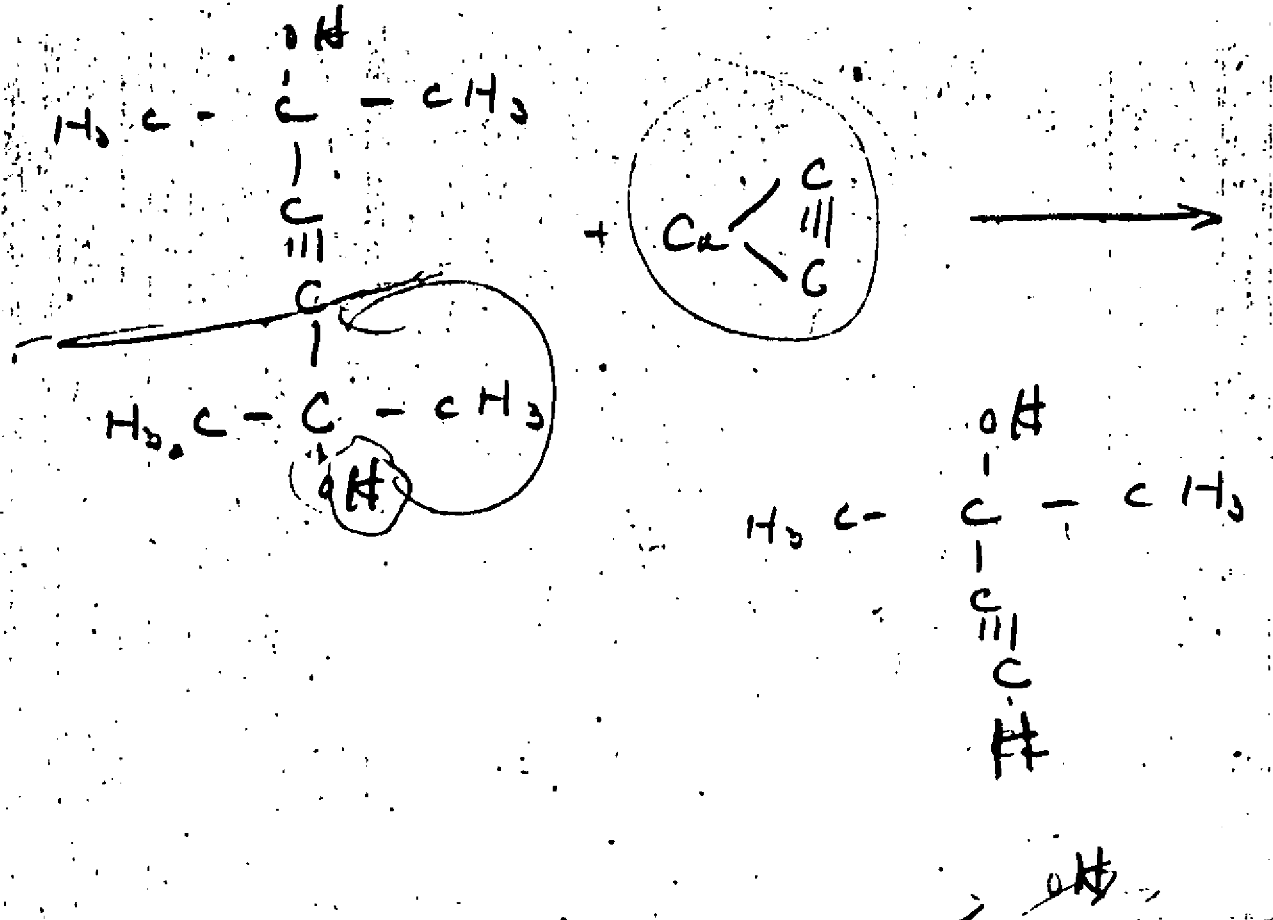
H
CH3
KC≡COH
KC≡CH
KOH
HOH
KOH
KC≡CH
HOH
KOH

THEORY #3

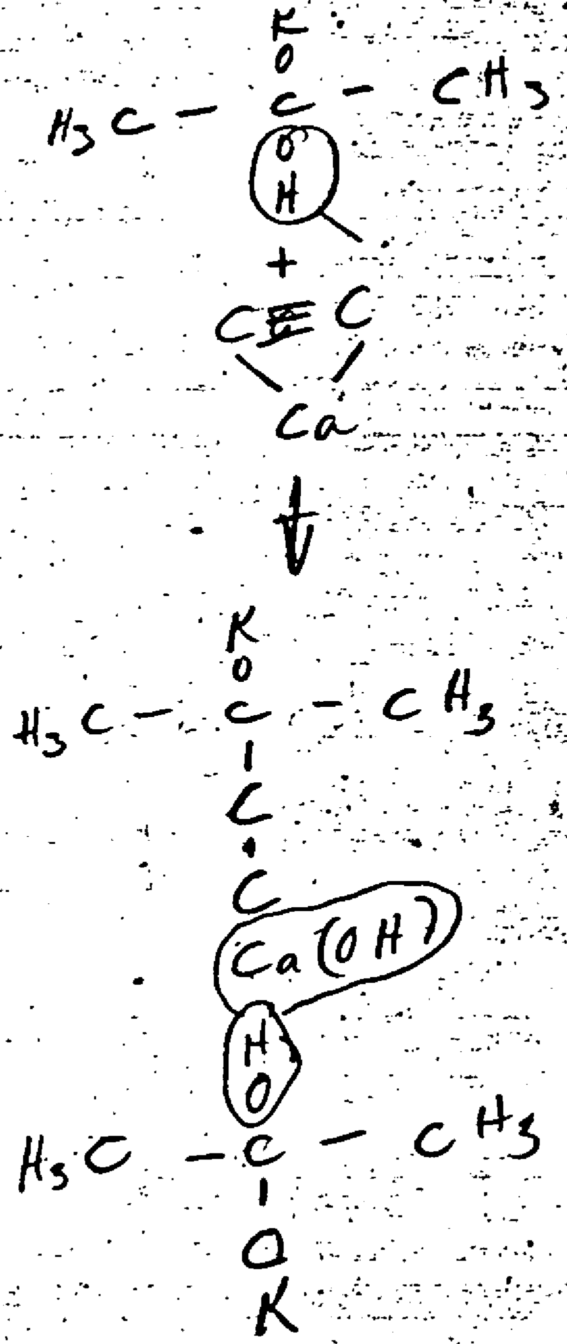


6/17/59

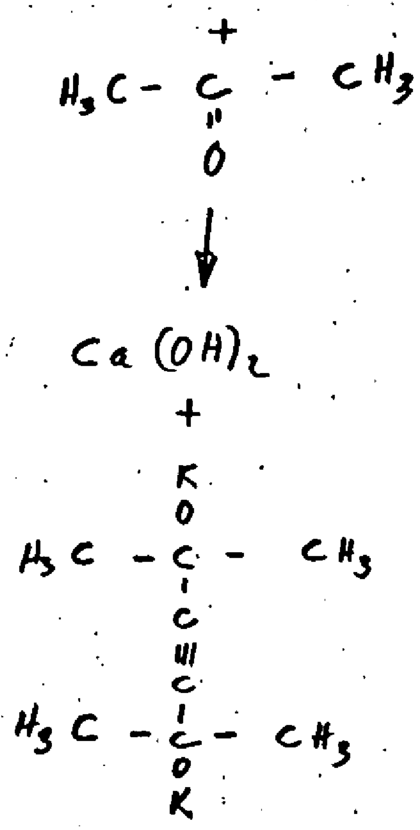
CH3

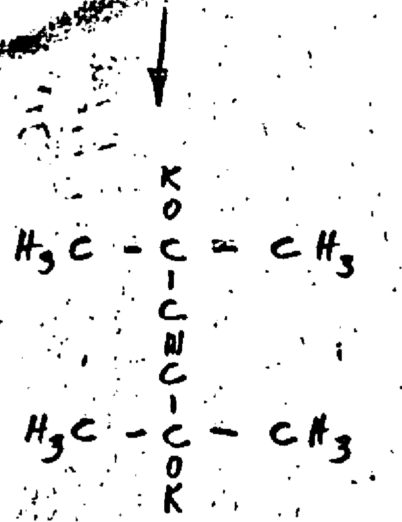


OH
H₃C - C - CH₃
C
C
H₃C - C - CH₃
OH
+
Ca C C
OH
H₃C - C - CH₃
C
C
H
OH



6/6/50


+
H₃C – C – CH₃
O
Ca (OH)₂
+
K
O
H₃C – C – CH₃
C
C
H₃C – C – CH₃
O
K



$$\ln \frac{p_2}{p_1} = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$2.3 \log p_2 - 2.3 \log p_1 = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\frac{\bar{3}.808}{-2.192} \qquad = -\frac{\Delta H}{R}\left(\frac{T_1 - T_2}{T_2 T_1}\right)$$

$$2.3 \log \frac{5}{760} = \frac{-10,100 \frac{cal}{mol}}{2 \frac{cal}{mol\,deg}}\left(\frac{479 - T_2}{479 \times T_2}\right)$$

$$\frac{2.3 \log .0067 \times 2 \frac{cal}{mole\,deg}(479^\circ)}{10,100 \text{ cal}} = -(479 - T_2)$$

~~cc atm~~ ~~mol deg~~

$$\frac{(-5.06)(2)(479)\,deg}{10,100 \frac{cal}{mol}} = \frac{-479 + T_2}{T^2}$$

$$(\;)\,T_2 + 479 = T_2$$

$$T_2(\;) - T_2 = -479$$

$$T_2 = \frac{-479}{(\;) - 1}$$

6/6/50

760 mm, 206°

$$\frac{dP}{dT} \quad \frac{\Delta H}{RT^2}$$

$$\begin{array}{r} 206 \\ 273 \\ \hline 479 \end{array} \qquad \begin{array}{r} 21 \\ 479 \\ \hline 479 \\ 958 \\ \hline 10059 \end{array}$$

$L = 21 \times 479 = 10{,}100$

$$\frac{dp}{dT} \quad \frac{Tds}{v} = \frac{dH}{v} = \frac{P\,dH}{RT}$$

$$\frac{dp}{dT} = \frac{P\,\Delta H}{RT}$$

$$\frac{dp}{dT} = \frac{\Delta H \cdot p}{RT^2}$$

$$\frac{dp}{p} = \frac{\Delta H}{R}\frac{dT}{T}$$

$$\int \frac{dp}{p} = \frac{\Delta H}{R}\int \frac{dT}{T^2}$$

$$\ln p = -\frac{\Delta H}{R}\frac{1}{T}$$

6/6/50
[illegible]

4^{50} - increase vacuum to 75 mm. - more H_2O coming over - then to 50 mm, very slow distillation - flask 105°, bath 121° -

5:00 Changed receiver
PH in dist flask 6.0

Press 50 mm

5:25 distillation at 50 mm & 56°C
Bath 135°C - Flask 119°C

6:00 Bath 150°C - " 136°C
Column 92°C

6.30 Col. 96° - Flask 145° - Bath 150°

6.40 " 65 (distillation slowed down)
Flask 145°C - Bath 158

6:50 Column 98°C - Flask 146 Bath 159

7:00 " 100°C

12-70

time.

11^{30} – 11^{45} – distils at 72-75° (3-4 mm
jacket 68°, flask 100°, bath 134°
fair rate, steady flow

11^{45} – 12^{00} – distils at 75°-82°
Jacket -71°, flask 105°, bath 140°
good rate

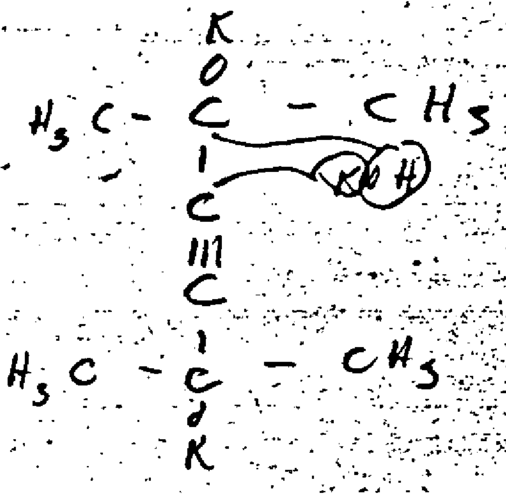
12^{05} – crystals appear in adapter
+ flask

$\cancel{2}K + \cancel{4}KOH \rightarrow K_2O + H_2$

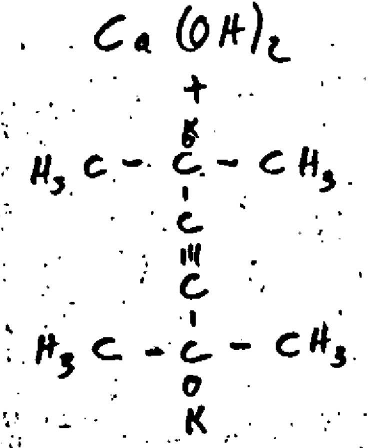
$2K + 2KOH \rightarrow 2K_2O + H_2$

3

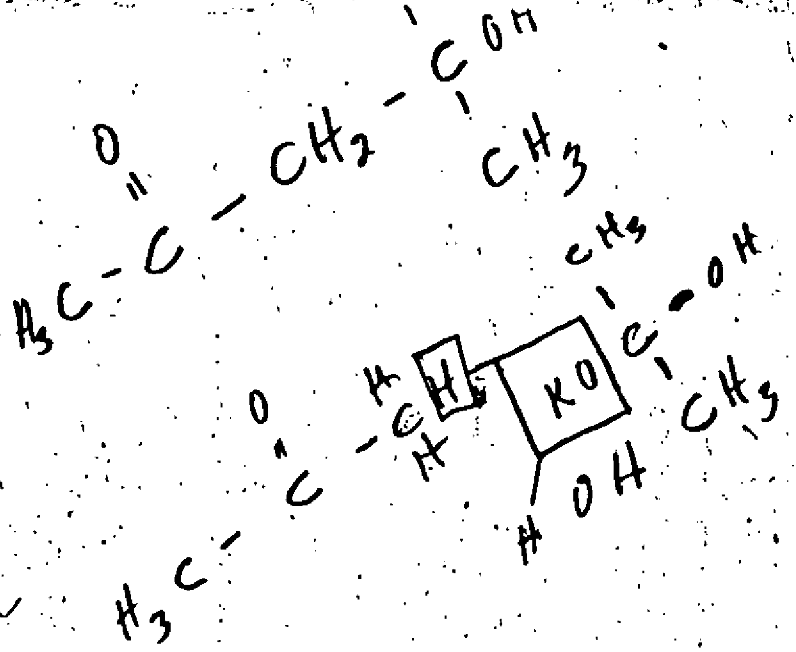
Ⓗ



6/6/50

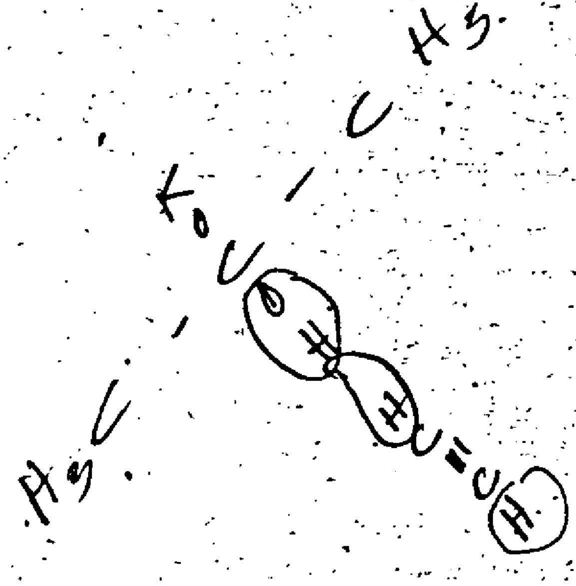


$Ca(OH)_2$
+
K
H_3C
CH_3
C
C
C
C
H_3C
CH_3
O
K

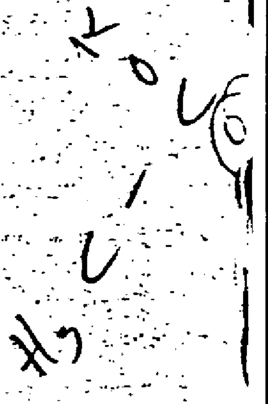


O
H_3C
C
CH_2
COH
CH_3
O
H
C
H
H
KO
CH_3
C
OH
CH_3
H
OH
H_3C

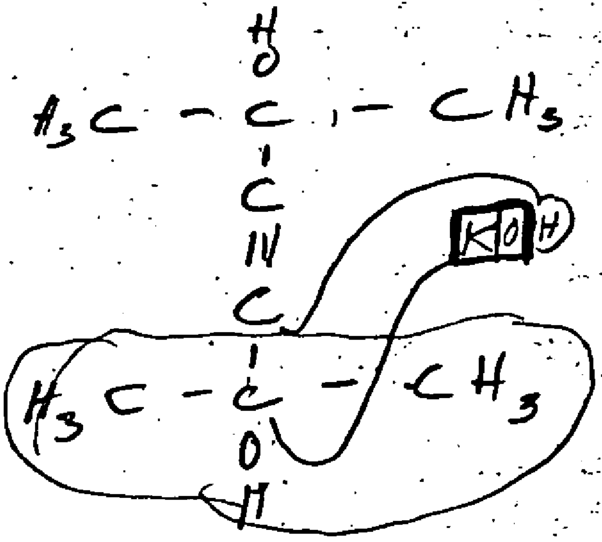
6/2/50



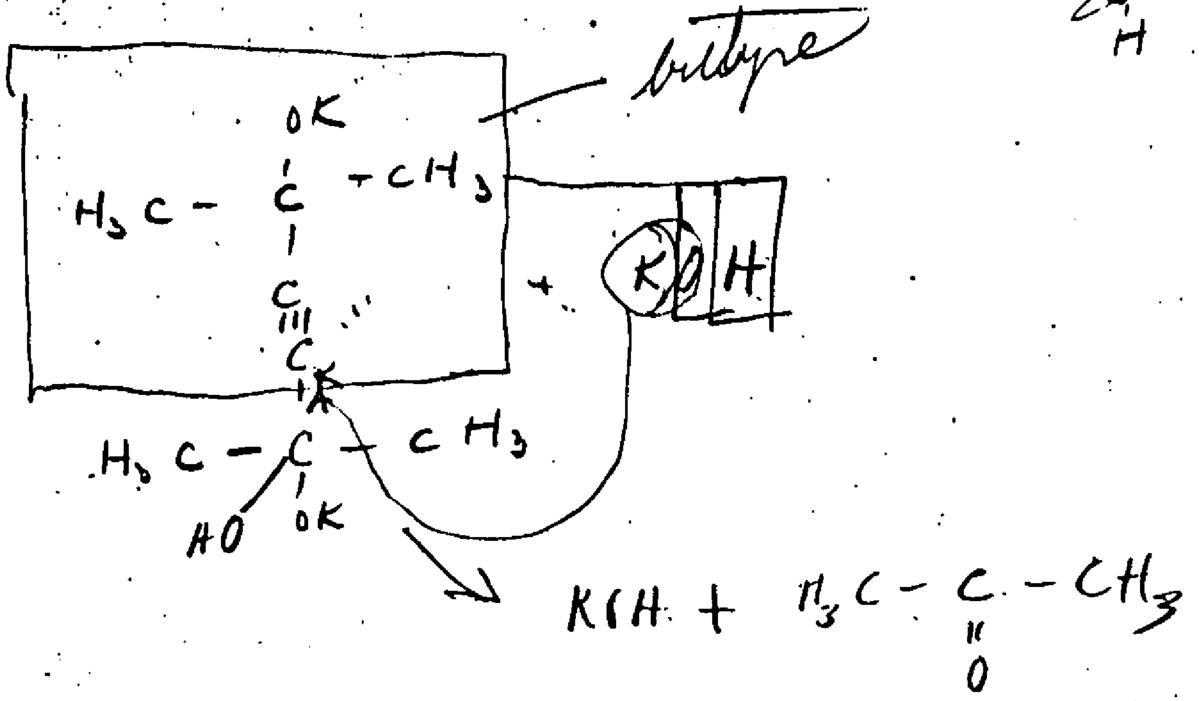
H3C
K
O
CH3
H
H
C
H

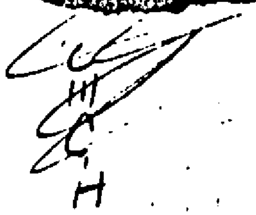


K
O
H3C

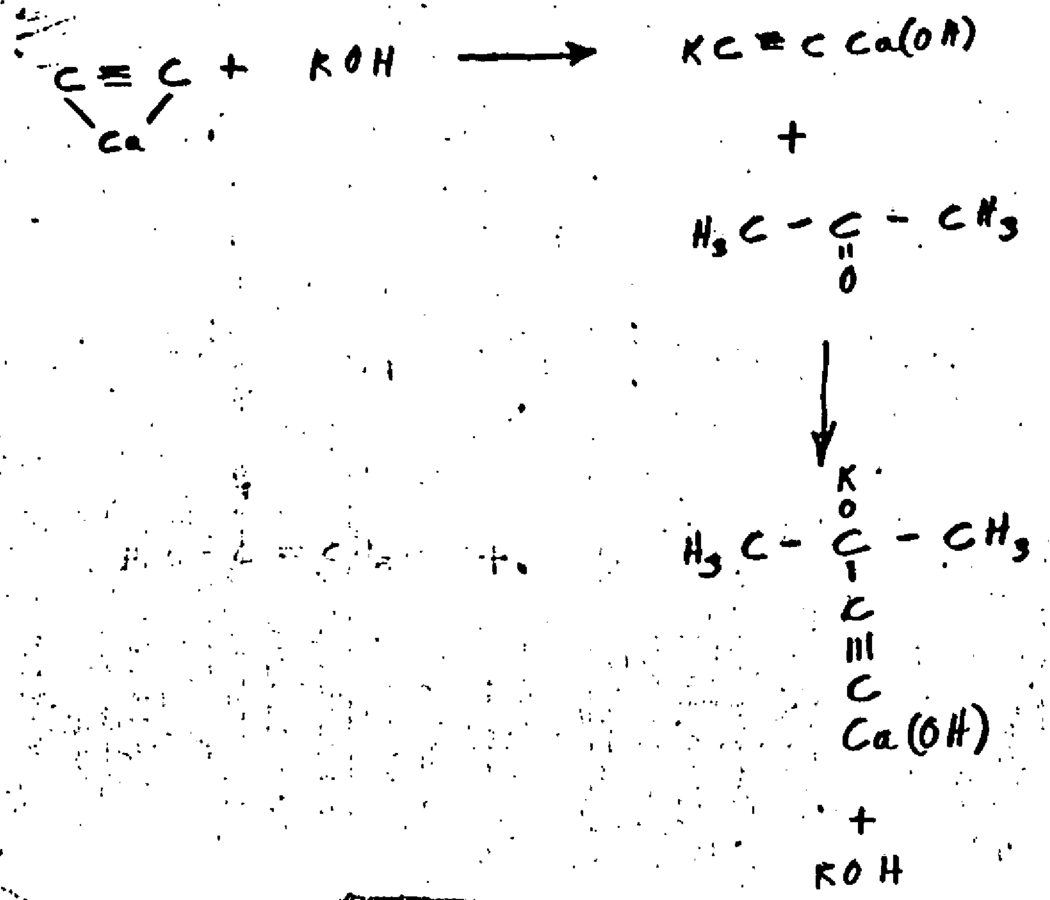


6/6/50

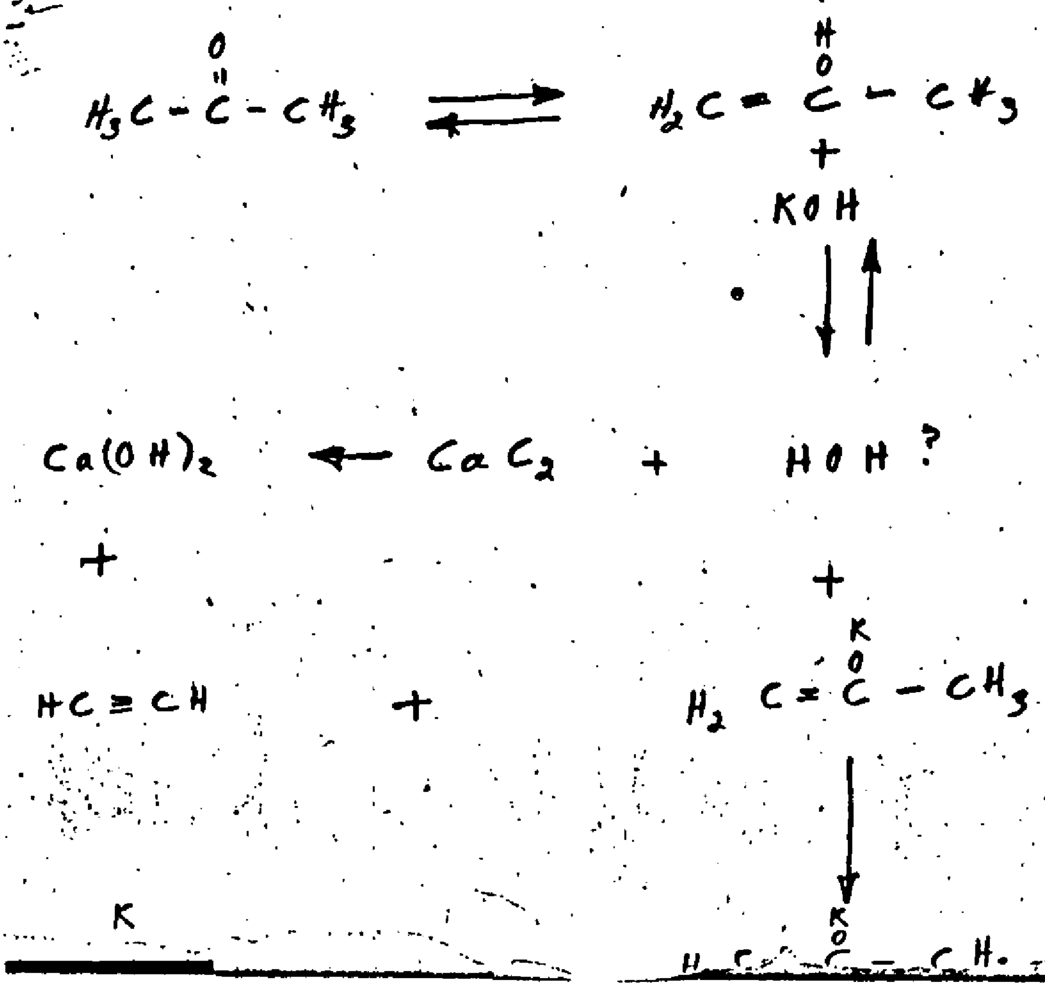

bildyne
OK
H3C – C – CH3
C
C
H3C – C – CH3
HO
OK
+
K O H
KOH + H3C – C – CH3
O


C
C
H

THEORY #2



THEORY #1



$$H_3C-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftarrows H_2C=\overset{\overset{H}{O}}{C}-CH_3$$

$$+$$

$$KOH$$

$$\downarrow\uparrow$$

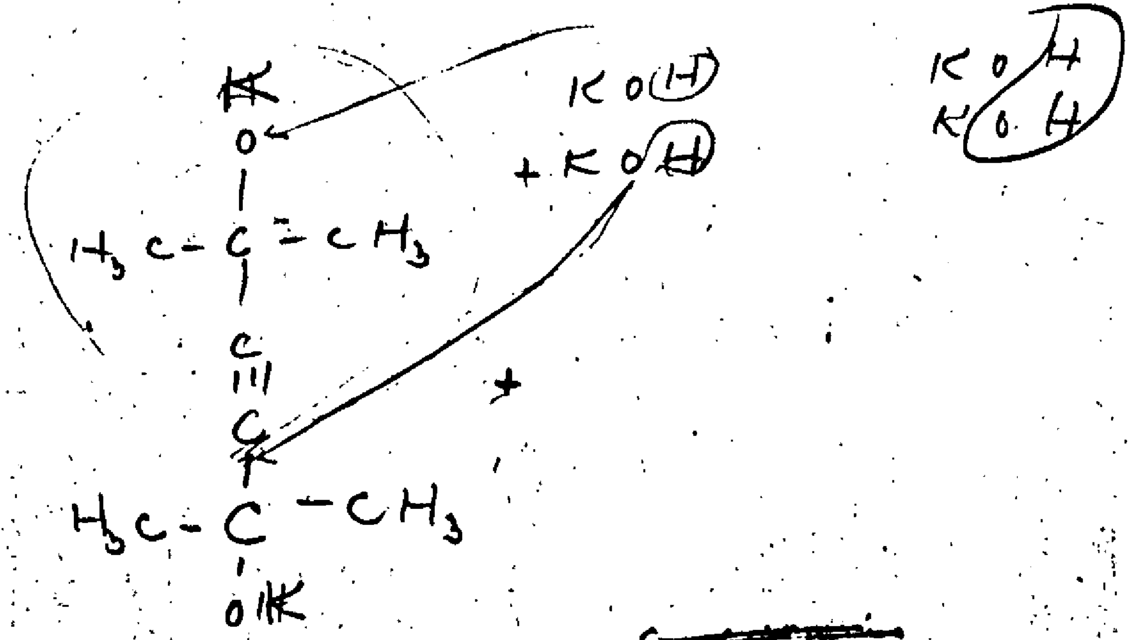
$$Ca(OH)_2 \leftarrow CaC_2 + HOH\ ?$$

$$+ \qquad\qquad +$$

$$HC\equiv CH + H_2C=\overset{\overset{K}{O}}{C}-CH_3$$

$$\downarrow$$

$$K \qquad H_2C=\overset{\overset{K}{O}}{C}-CH_3$$



~~[illegible]~~

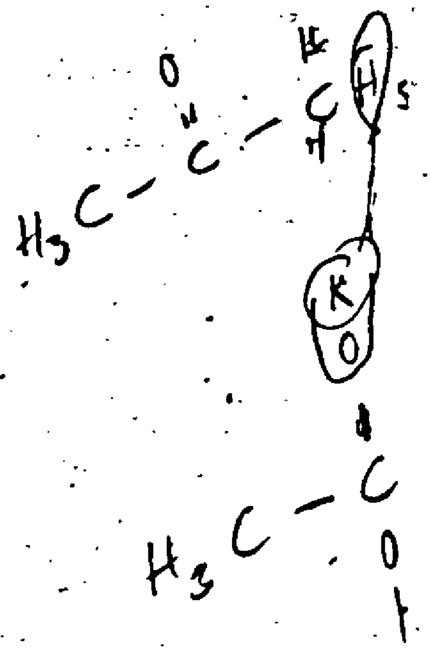
5/9/19 Butinol

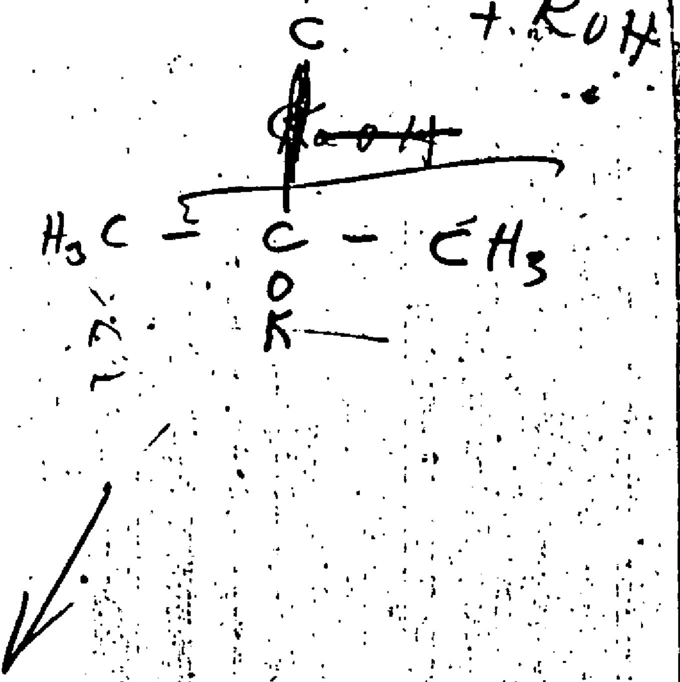
Identine

~~[illegible]~~ mil

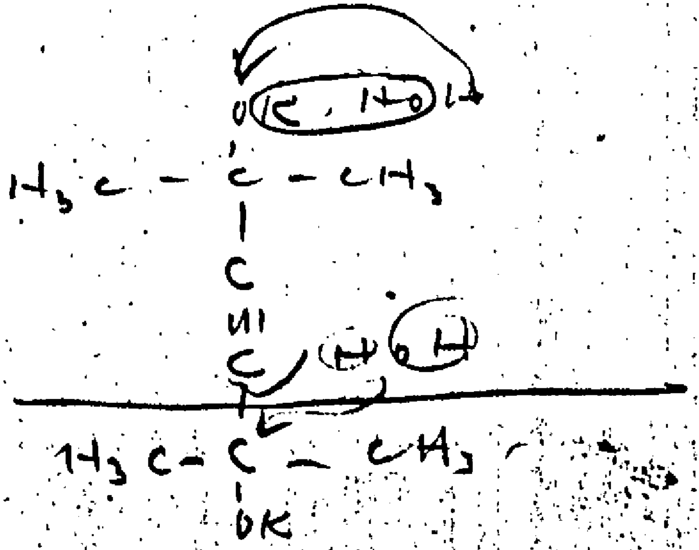
[illegible]

[illegible]

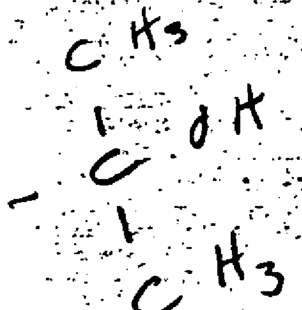

O
H
C
H
s
H3C
C
K
O
C
H3C
O


C
+ KOH
~~CaOH~~
H3C
C
CH3
O
K

	mol	2 mol (based on acetone)	mol
	mol	2 mol	mol
			None
Et_2O	150 cc	100 + 70 cc	
Time addition	1.5 hrs	1 hr	
added react	2 hrs		
Stand	overnight		



6/6/56



$$\begin{array}{c} CH_3 \\ | \\ -\,C\;OH \\ | \\ CH_3 \end{array}$$

$$2.303 \times \log \frac{60}{760} = (4.19 \times 10^3)(2.72 \times 10^{-3}) - \frac{4.16 \times 10^3}{T_1}$$

$$2.303\,(0.9102)\,T_1 = 11.39\,T_1 - 4.16 \times 10^3$$

$$\begin{array}{r} 2.10 \\ 11.39 \\ \hline 13.49\;T_1 \end{array} = 4.16 \times 10^3$$

$$T_1 = 36°\,C$$

$$\begin{array}{r} 0.0197 \\ \hline 0.910 \end{array}$$

	Press	Temp °C
acetone	100	7°
Butane	100	36 (38-41 actual)
H_2O	100	51
Hexane	100	128
	20	124 (112-[illegible] actual)
acetone	400	22
	200	22
Butane	~70	54°

The second group in turn may be div into two sub groups, the first of which is related to those reactions methods in which sodium or ~~calcium~~ potassium acetylide first takes place and then acts on acetone. [Ber 51. 377 (1918)]

On the other hand, the methods comprising the second sub-group are characterized by the reaction between sodium or ~~calcium~~ potassium first ~~and~~ ~~with~~ acetone followed by the action of acetylene on A. However, as is evident from the review of the literature in this article as well as from recent researches of U. Karoterse(?) and D. Koffman, all methods of synthesis of acetylenic alcohols are most ~~unsatisfactory~~ disadvantageous, due especially to poor yields. From the articles referred to it is evident that by the existing methods of synthesis of acetylenic alcohols the yields do not exceed 36% of the theoretical. It remains to recall the idea of the above mentioned authors that the methods developed up to this time for the synthesis of acetylenic alcohols and in particular 3-methyl-3-hydroxy-1-butine are more elegant than practical, in spite of the fact that further work on 3-methyl-3 hydroxy-1-butine, for example its dehydration and ~~subsequent~~ the resulting chloroprene does not offer any difficulties

J. Gen. Chem. 4: 1347-57 (1934)
(Kazarian)
New Method of Applying Calcium Carbide

For some applications in our laboratory it was necessary for me to prepare methyl chloroprene. From literature [J. Am. Chem. Soc. 54: 4071 (1932)] it was known to me that methyl chloroprene could be prepared from 3-methyl-3-hydroxy-1-butine by dehydration, with the ensuing compound ~~combination~~ (~~station~~) ~~with~~ HCl with the iso-propenyl acetylene ~~acetone~~ obtained from the dehydration (operation).

As far as it concerns 3-methyl-3-hydroxy-1-butine ~~is concerned~~ and acetylenic alcohols in general, that besides the above mentioned purpose, find their use in other applications, as for example, for the preparation of soporific substances such as iso-propenyl propargyl, iso-propyl-barbituric acid [Cbl II, 1823 (19 the preparation of which has been known since 1914 [Cbl II, 1870 (1914)]

All accounts of separate investigations and of patents [Bull (3) 30, 210 (1903)] about the methods of their preparation can be divided into two basic ~~fundamental~~ groups. In the first group belongs the preparation of acetylenic alcohols by means of acetylenic compounds ~~action~~ union (or combination) of magnesium and aldehydes and ketones [Cbl II 1870 (1914

In addition to what has been said, in the aforementioned methods of obtaining acetylene alcohols the following ~~elements~~ substances are used: organic compounds of Magnesium, Sodium or Potassium acetylenide, sodium compound of acetone obtained thru constant mixing during 5 hrs of powdered sodium amide + acetone in a ether medium at 10-20°. All that undoubtedly raises the cost of (3) metyl-butene (1)-(3) hydroxy.

methyl methacrylate

alkyl ketone

in Germany, as is shown by Schaller (1) [Ber 55, 2903 (1922)] ~~who~~ the technical 3-methyl-3 hydroxy-1-butene on ~~which he~~ that he used in his experiments contained 20% chlorbenzene, which apparently has been used as a solvent in the processing of 3-methyl-3-hydroxy-1-butene.

However, these methods did not appear to us applicable all, and I therefore it was necessary to find a new more efficient method of synthesis of 3-methyl-3-hydroxy-1-butene and only after that go over to the making of methyl chloroprene.

As was pointed out above, in all the methods of synthesis of acetylenic alcohols, either free acetylene is used or in form of an acetylenide (Mg, K, Na)

The method proposed by me consists of the fact that the reaction with acetone is not thru acetylene or acetylenide obtained from it but thru calcium carbide ~~is used~~ directly. As it became clear from my experiments, calcium carbide which up to this time was considered as an active metal organic compound only in relation to water

To what has been already said we may add that in the above mentioned methods of preparing acetylenic alcohols applications are made of such substances as magnesium-organic compounds, sodium or potassium acetylides, sodium compound of acetone, obtained from triturated sodium and acetone in the ether medium at 10-20°C under constant stirring during a period of 5 hrs. All this definitely increases the cost of 3-methyl-3-hydroxy-1-butine.

it was shown that

Moreover, in the whole range of methods, ~~the formations~~ ~~appearing~~ obtained in the course of reactions ~~of~~ alcoholates of acetylenic alcohols are decomposed by acetic acid; instead of theoretically required 58 g (1 gm-mole) of acetone, 306-320 gm. is used up. Finally in case sodium amide is used the reaction is prolonged to 12 hrs, the apparatus is complex and considerable loss of acetylene takes place as acetylene ~~leave out~~ is continuously during the 7 hrs. under ~~the~~ pressure of 0.5 atm. ~~Nevertheless~~, Regardless of the enumerated numerous shortcomings of the methods ~~for~~ of synthesis of acetylenic alcohols in general and 3-methyl-3-hydroxy-1-butine in particular ~~the~~ ~~the~~ latter compound [illegible] the process of manufacture.

has the following advantages over the existing methods:

(1) appreciable simplification of apparatus since we eliminate the apparatus for obtaining acetylene from CaC_2, also a whole row of washing ~~the~~ flasks, ~~which~~ necessary for the purification of acetylene.

(2) The expensive sodium amide is substituted by cheap calcium hydroxide & by still cheaper sodium hydroxide.

(3) In the new method ~~the~~ (minute) powdered carbide is used. ~~for~~

(4) The amount of applied acetone is diminished by six times since in my method one gm-mole (58gm) of acetone is used instead of the present 300 gm.

(5) The duration of the reaction is appreciably cut down, instead of 12 hrs, in my method it takes only 2-3 hrs. ~~and for~~

(6) And finally, the most substantial advantage of the new method is the appreciably increased yield: 70% against the existing 36% of the theoretical.

~~it was~~ proved itself ~~[illegible]~~ able to be activate it even in the cold by mixing it well with finely powdered dry potassium or sodium hydroxide (the action of other bases is still being investigated) which gives a reaction with acetone (reactions with other ketones and aldehydes are also being investigated). ~~The~~ Hydrolitically dissociation of the product of reaction obtained with water only results in acetylenic alcohols, namely 3-methyl-3 hydroxy-1-butine and 2,5-dimethyl-2,5-dihydroxy-3-hexine. From the account of the experiments described below it became known that using the same reactants, namely ~~potassium~~ calcium carbide, potassium hydroxide and acetone ~~but~~ but by just varying the conditions of the experiments it is possible to obtain either almost ~~absolutely~~ entirely a yield of 70% of theoretical 3-methyl-3-hydroxy-1-butine or almost two absolutely 2,5-dimethyl-2,5-dihydroxy-3-hexine with a yield of 74% of the theoretical. Incidentally, the latter while using sodium amide instead of 1 gm-mole (144 gm) yields only 2 g which represents 1.37% of the theoretical yield.

Assuming that the decomposition of ③ CaC₂ and water takes place gradually & and the first reaction follows:

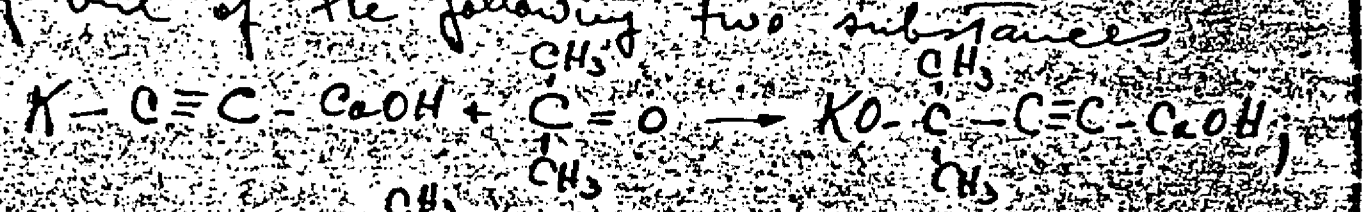
$$CaC_2 + H_2O \rightarrow H-C\equiv C-CaOH$$

I simultaneously assumed that potassium hydroxide must react with calcium carbide in the similar way

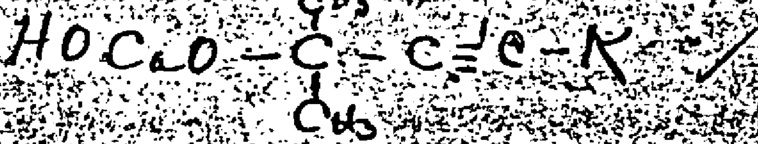
$$CaC_2 + KOH \rightarrow K-C\equiv C-CaOH$$

~~This scheme of reaction is proven by the fact that in order the necessity to add to the reaction with acetone of one~~

The above scheme of reaction is proven by the fact that 1 gm mole of Potassium Hydroxide is sufficient to introduce 1 gm mole of Calcium Carbide into the reaction of Acetone. Consequently, the reaction of the formation of 3 methyl butine (1), (3) hydroxy from Calcium Carbide, Pottassium hydroxide & acetone brings first about the formation of one of the following two substances



$$K-C\equiv C-CaOH + \overset{CH_3}{\underset{CH_3}{C}}=O \rightarrow KO-\overset{CH_3}{\underset{CH_3}{C}}-C\equiv C-CaOH;$$



$$HOCaO-\overset{CH_3}{\underset{CH_3}{C}}-C\equiv C-K$$

Besides that in the performance ~~of~~ by my method we eliminate the cooling of the reaction mixture from 10-20°C which cuts down on the expense of ether. Instead of the usual 2 liters we use only 200 gm. of ether and finally for the hydrolytic dissoliation of the products of reaction, we use plain water instead of the acetic acid.

Theoretical Part

As stated above in the method I proposed, acetylenic alcohol is obtained by adding acetone in an ether medium to a powdered mixture of calcium carbide and potassium or sodium hydroxide, and further final hydrolytic dissociation of the product of reaction.

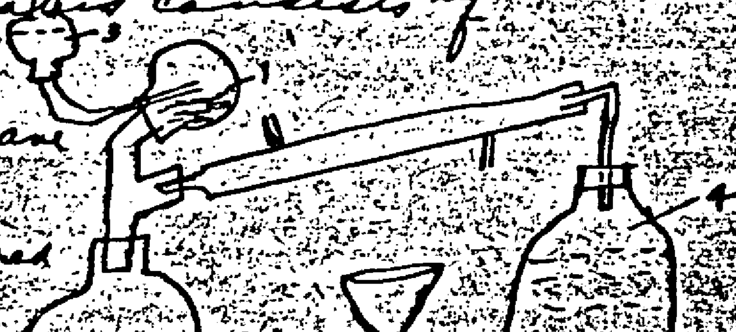
The reason for my investigation of this reaction with CaC_2 still needs a check ~~of~~ by experiment. However, independent of ~~that~~ the degree of justification of my considerations, they already gave practical results ~~in that~~ namely that the new practical and ~~a~~ simple method of obtaining acetylenic alcohols such as 3-methyl-3-hydroxy-1-butine and 2,5-dimethyl-3,4-dihydroxy-3-hexine.

reacts not with CaC_2 but with Acetone giving potassium-acetone. This reaction is due to the taking away of water by the action of carbide. Then the formed acetylene or ~~distilled~~ the still partly hydrolyzed potassium carbide, the formation of which was [illegible] assumed above, combining with potassium-acetone gives substances the result of hydrolysis of ~~whose~~ which are 3-methyl-3-hydroxy-1-butine and 2,5-dimethyl-2,5-dihydroxy-3-hexine. We are continuing in the laboratory tests to check the explanation of this mechanism.

Experimental Part

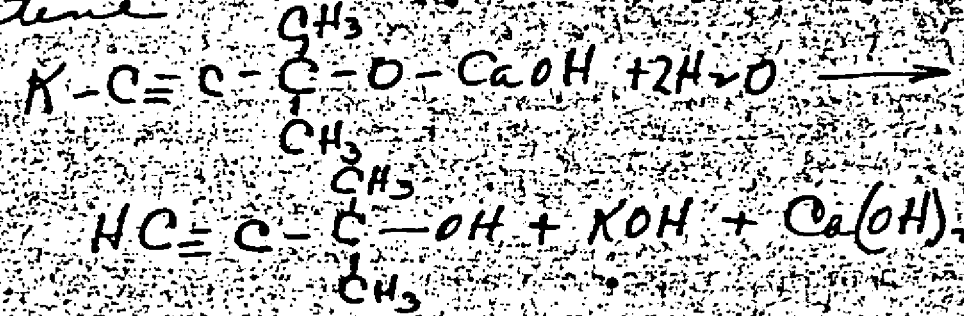
Test I Simultaneous formation of 3-methyl-3-hydroxy-1-butine and 2,5-dimethyl-2,5-dihydroxy-3-hexine

The apparatus consists of



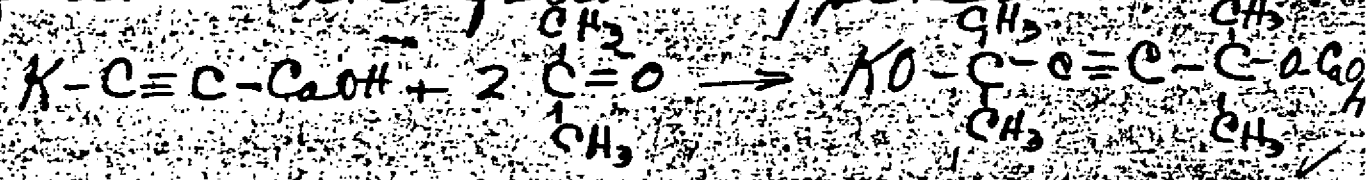
retort (1) in ~~where we have which a~~ a mixture of finely powdered 1 g-mole of potassium hydroxide and CaC_2, ~~containing~~ equivalent to 1 gm-mole of acetylene,
1) retort (2), containing about 400 g. of acetone;

which is further ~~[illegible]~~ decomposed (7)
by water, giving ~~#~~ 3-methyl-3-hydroxy-1-butine



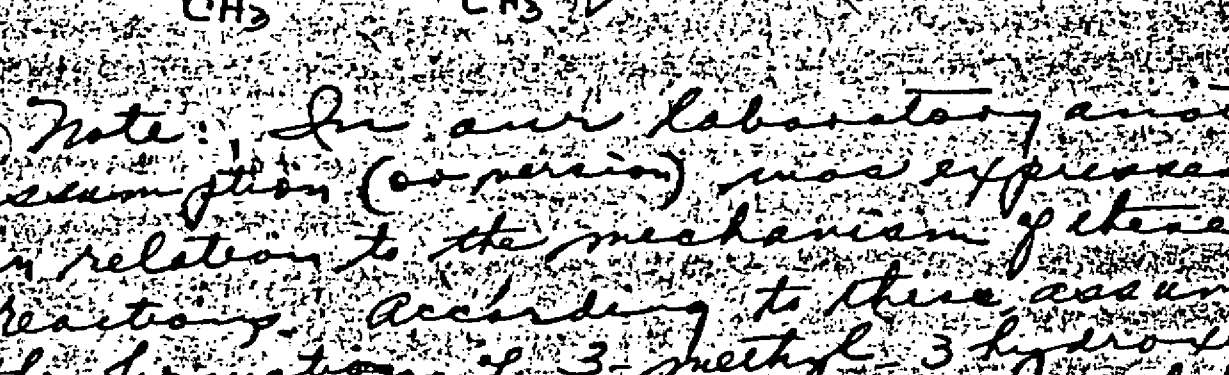
$$K-C\equiv C-\overset{CH_3}{\underset{CH_3}{C}}-O-CaOH + 2H_2O \longrightarrow HC\equiv C-\overset{CH_3}{\underset{CH_3}{C}}-OH + KOH + Ca(OH)_2 \checkmark$$

In the case, however, of formation of 2,5-dimethyl-2,5-dihydroxy-3-hexine ~~and~~ the first part of the reaction remains unchanged, and the further reaction follows the following scheme:



$$K-C\equiv C-CaOH + 2\,\overset{CH_3}{\underset{CH_3}{C}}=O \longrightarrow KO-\overset{CH_3}{\underset{CH_3}{C}}-C\equiv C-\overset{CH_3}{\underset{CH_3}{C}}-OCaOH \checkmark$$

Through the hydrolytic dissociation of the product of reaction the following is obtained: 2,5-dimethyl-2,5-hydroxy-3-hexine



$$KO-\overset{CH_3}{\underset{CH_3}{C}}-C\equiv C-\overset{CH_3}{\underset{CH_3}{C}}-OCaOH + 2H_2O \longrightarrow OH\overset{CH_3}{\underset{CH_3}{C}}-C\equiv C-\overset{CH_3}{\underset{CH_3}{C}}-OH + KOH + Ca(OH)_2^{*} \checkmark$$

(*) Note: In our laboratory another assumption (conversion) was expressed in relation to the mechanism of these reactions. According to this assumption the formation of 3-methyl-3-hydroxy-1-butine and 2,5-dimethyl-2,5-dihydroxy-3-hexine was explained as follows:

After the decomposition by water the the following three layers strata are formed

(1) Acetone solution of 3-methyl-3 hydroxy-1-butine ~~and~~ 2,5-dimethyl-2,5-dihydroxy-3-hexine.

(2) The water layer in which the substances of the first layer are dissolved especially 2,5-dimethyl-2,5-dihydroxy-3-hexine.

(3) Residue.

The contents of the flask was filtered ~~through~~ and washed first with a small quantity of water and then with ether after which ~~the filtrate~~ the acetone layer was separated from the water layer in the filtrate by means of a ~~dividing~~ separatory funnel. The water layer, after being neutralized with hydrochloric acid and saturated with sodium chloride was extracted by means of a small amount of ether while the latter was added to the main acetone solution.

After ~~the~~ drying the acetone-ether solution passed through a filter on an oil bath. A after fraction filtered through ~~ha~~ at 95-100°C consisted of 3-methyl-3 hydroxy-1-butine, which ~~and~~ ~~which~~ gave with an ammonias silver solution ~~with~~ a silver white voluminous residue of silver salt. ~~For~~ So, for instance [illegible] acetylene 1.5 am. of the above

(excess of acetone is taken as a solvent), ⑪
funnel (3) in which 300 g of water are placed
and finally gasmeter (4).

Retort (2) is cooled initially with ice-water and then filled with pulverized mixture of CaC_2 and KOH in ~~with~~ small amount ~~of~~ at a time during 1 hrs transfer, from retort (1) to the acetone of retort (2). Retort (2) is connected ~~with~~ to the gas meter through a condenser, in order to return to the reaction retort any evaporated acetone which might occur due to the heat of the reaction. The gas meter serves for the determination of the quantity of acetylene formed during
? the breakup of the contents by the water. After the entire given amount of potassium hydroxide and calcium carbide was placed in the acetone, the reaction mixture has been left in the same condition for another two hrs. for the completion of the reaction. After 2 hrs, 300 g of water from dropping funnels had been put in the reaction flask for the decomposition of products of reaction as well as of the non-reacted carbide. Nevertheless the amount of acetylene separated during the decomposition was so negligible that it can be disregarded, and we
we thus consider that practically the

After the decomposition by water the (1)
the following three layers strata are formed

(1) Acetone solution of 3-methyl-3 hydroxy-1-butine and 2,5-dimethyl-2,5-dihydroxy-3-hexine

(2) The water layer in which the substances of the first layer are dissolved especially 2,5-dimethyl-2,5-dihydroxy-3-hexine

(3) Residues.

The contents of the flask was filtered ~~through~~ and washed first with a small quantity of water ~~and~~ then with ether after which ~~the filtrate~~ the acetone layer was separated from the water layer in the filtrate by means of a ~~dividing~~ separatory funnel. The water layer, after being neutralized with hydrochloric acid and saturated with sodium chloride was extracted by means of a small amount of ether while the latter was added to the main acetone solution.

After ~~the~~ drying the acetone-ether solution passed ~~through~~ into a filter on an oil bath. A fraction filtered through ~~ha~~ at 95-100°C consisted of 3-methyl-3 hydroxy-1-butine ~~and~~ which ~~which~~ gave with an ammoniac solution of silver ~~with~~ a silver-white ~~voluminous~~ bulky residue of silver salt. ~~For~~ So, for instance (with) acetylene 1.5 gm. of the above [illegible]

(100 g) contained 1 gm-mole acetylene. Also added 150 gm. of ether dried on calcium chloride. To this mixture during 1.5 hrs gradually were added 58 g of acetone. ~~The~~ During that time the reaction mixture was well mixed and cooled with ice-water. While adding the acetone, it was noticed that the ether layer is colored and the residue solidified. After adding the whole given amount of acetone, the reaction mixture from time to time was stirred during 2 hrs, after which it was left undisturbed in ice-water until the next day. The next day the well cooled reaction mixture was subjected to hydrolysis with 150 cc. ice-water.

After the decomposition the faintly colored ether solution was separated from the water layer and the residue, the residue filtered and washed first with water and then several times with ether. The water filtrate after being neutralized with hydrochloric acid and saturated with sodium chloride was extracted with ether and the latter added to the main ether solution. After drying over calcium chloride, the ether solution was filtered in an oil bath with good defleg-

⑬

3.05 g. of silver salt of 3-1 ethyl-3 hydroxy 1-butine instead of the theoretical 3.44 g. This fraction weighed 51 g. Thus taking into consideration that the sample of this fraction gave silver salt 3.05 g instead of the theoretical 3.44 g. the resulting yields of 3-methyl-3 hydroxy-1-butine ~~equals~~ was 61.36 % of the theoretical

The next fraction filtered through at 198-200°C after a certain amount of settling, crystallized. The cleaned crystals weighed 18.5 g. and had a melting pt. of 94°C, the corresponding to the melting point of 2.5-dimethyl-2.5-dihydroxy-3 hexine as shown in the literature. 2.5-dimethyl-2.5-dihydroxy-3 hexine is ~~are~~ well soluble in water. It crystallized well out of toluol and Xylol ~~due~~ which helped to obtain the crystals in sizes ~~5.7~~ 5.6 cm. by 0.5 cm. The yield of this figured on an amount of acetone which which did not enter into the ~~the~~ ~~th~~ composition ~~formed~~ of 3-methyl-3 hydroxy-1-butine formed represents 34.5 % of the theoretical yield

Test 2 Obtaining 3-methyl-3 hydroxy-1-butine

In a 2 liter round bottom flask was preliminarily placed pulverized mixture: [illegible] potassium hydroxide

Test 3. Obtaining 2,5 dimethyl-2,5 dihydroxy
~~[illegible]~~ 3-hexine

To the mixture of 100 cc. of ether dried over $CaCl_2$ and the pulverized 100 g of CaC_2 and 56 g of KOH in the 2-liter round bottom flask was added in 1 hr. in small quantities from the dropping funnel 58 g. of Acetone. During this addition the reaction mixture was well stirred and the inside ~~the~~ temperature was kept from beginning to end at 6-7°C. To eliminate the ~~hardening~~ solidification of the reaction mixture, which would prevent thorough stirring, 70 cc. ~~[illegible]~~ of ether were added. After the ~~addition~~ pouring in of all the acetone the reaction mixture was stirred from time to time during 3 hrs. ~~and~~ Towards the end of the reaction the reaction mixture which was at a temperature of 13-15°C started to ~~to redden~~ turn faintly red and swell and finally solidified. All this has not been observed in the test No 2 while obtaining 3-methyl-3 hydroxy-1-butine. The next day the product of the reaction at ~~[illegible]~~ 7°C was decomposed with 150 cc. of water. After separating the ether layer from the residue the latter at 90-98°C 60 gm. of 3-[illegible]ethyl-3 hydroxy-1-butine was distilled ~~filtered~~ giving with ammoniate solution of silver nitrate a white explosive residue of silver salt. The composition of the fraction 110-200°C weighing 2 g so far has not been analyzed or investigated. Finally above ~~over~~ 200°C was distilled ~~filtered~~ ~~fo~~ 4 more grams of tarred and non-crystalized substances. To acertain that the fraction distilled ~~filtered~~ ~~at~~ out at 90-98°C was actually 3-methyl-3-hydroxy-1-butine, ~~a~~ a quantitative analysis was made to determine the silver in the residue of the silver salt. A definite ~~The calculated~~ quantity of the residue was decomposed by nitric acid free of chlorine and in the obtained solution the presence of silver was established by ~~through~~ accepted ~~regulator~~ method of weighing analysis. If we assume that one molecule of 3-methyl-3-hydroxy-1- ~~hexine~~ butine reacts with one molecule nitrate then out of 0.2770 g. of silver salt of 3-methyl-3-hydroxy-1-butine we should have 0.2788 g. silver nitrate — 0.1564 g of silver — 100% we obtained 0.2043 g. silver nitrate — 0.1537 g silver

~~of the~~ From the water filtrate the (2, dissolved 5 dimethyl-2,5 hydroxy-3-hexine was extracted with ether after acidifying with HCl and saturating with NaCl. All the ether solutions obtained after drying over $CaCl_2$ & were distilled in an oil bath. & 3-methyl-3-hydroxy-1-butine came out only 3 g.

~~The crude~~ 52 g of crude, not crystallize 2,5 dimethyl-2,5 dihydroxy-3-hexine were obtained, that is 74% of the theoretical yield, based on acetone. The crude product may be ~~refined~~ purified with ordinary benzene. The melting point of the purified 2,5-dimethyl-2,5 dihydroxy-3-hexine is 94°C.

Patented Apr. 20, 1943 2,317,138

UNITED STATES PATENT OFFICE

2,317,138

GRANULAR POLYMERIZATION OF ETHANOID MONOMERS

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No Drawing. Application July 23, 1940,
Serial No. 346,895

7 Claims. (Cl. 260—23)

This invention relates to the manufacture of molding compounds having an ethenoid resin base and, more particularly to the incorporation therein of lubricants for the purpose of preventing their adhesion to metal molds.

In the formulation of plastic molding compounds it is customary to incorporate therein small proportions of substances which serve to facilitate the removal of molded articles from molds by preventing the adhesion of the compound to molds. Such substances are designated "mold lubricants" or simply "lubricants."

The incorporation of lubricants in molding compounds having an ethenoid resin base, such as molding compounds comprising the polymers of methyl methacrylate and its homologues and interpolymers in which such polymers predominate, has given rise to certain difficulties. It is the preferred practice to produce these polymers by the so-called granulation process in which the material to be polymerized is suspended in the form of small droplets in an inert liquid, usually water, and polymerized therein so as to yield corresponding small globules or granules of polymer. Several different methods of effecting the incorporation of lubricant have heretofore been used.

One procedure is to select a lubricant which is soluble in the monomeric material, and to dissolve the lubricant in the monomer before subjecting the latter to polymerization. This procedure has been used without difficulty in the case of certain lubricants of neutral character, such as long-chain aliphatic alcohols, butyl stearate, ethyl palmitate, and natural waxes, which are, however, of only mediocre effectiveness as lubricants. With lubricants of acidic character this procedure gives rise to mechanical difficulties during the course of the polymerization, i. e., objectionable aggregation of the globules, or objectionable foaming of the aqueous vehicle, or both.

Another procedure defers the addition of the lubricant until after the completion of the polymerization. At this time, with the polymerization batch at a temperature higher than the melting point of the lubricant, the latter is added to the batch under vigorous agitation. By this means are obviated the two difficulties mentioned in the first described procedure but the deposition of the lubricant upon the globules of polymer is uncertain and incomplete; much of the lubricant is subsequently drained away with the water and only an uncertain fraction of it remains with the polymer.

Still another procedure defers the addition of the lubricant until the polymer in globular form has been dried, whereupon the lubricant is incorporated with it by kneading upon mixing rolls or their equivalent, conveniently at the same time at which color ingredients, if any, are to be incorporated. This procedure, carefully carried out, insures the presence of the desired proportion of lubricant in the compound and its proper distribution therein, but is a source of added expense. The rolling operation is complicated and prolonged by the lubricating effect of the lubricant thus added; the lubricating effect delaying the formation of a coherent mass which will adhere satisfactorily to the surface of the rolls and so become capable of being effectively kneaded. And if no other ingredient is to be incorporated, this procedure involves the addition of the step of rolling solely for the purpose of incorporating the lubricant.

An object of the present invention is to formulate and to produce molding compounds having an ethenoid resin base, particularly those having a base of polymers of methyl methacrylate and its homologues, or of copolymers in which these polymers are predominate components, which molding compounds are effectively lubricated so that they will not adhere to metal of molds in the course of ordinary molding operations. A further object of the invention is to provide a method whereby effective lubricants can be incorporated into molding compounds of this character without the difficulties above recounted, i. e., a method in which the process of polymerization is not complicated by aggregation of globules nor by foaming of the liquid vehicle, and in which the step of kneading on rolls is not delayed and prolonged by an unwanted lubricating effect. It is further an object of the invention to provide lubricants adapted to be incorporated without these difficulties and possessing properties desirable in a lubricant, namely, absence of deleterious effect upon the color, the transparency, and the homogeneity of articles molded from the resulting compound, effectiveness as lubricants when used in small proportions, and absence of appreciable depressing effect upon the softening temperature of these compounds. Other objects will be apparent from the description of the invention given hereinafter.

The above objects are accomplished according to the present invention by polymerizing an ethenoid monomer dispersed in water containing a dispersing agent and adding to the dispersion during the peak period of the polymerization reaction a lubricant selected from the group consisting of the saturated aliphatic acids containing 12–18 carbon atoms, inclusive, and the di- and tri-substituted esters of phosphoric acid with saturated aliphatic alcohols of 12–18 carbon atoms, inclusive.

Lubricants coming within the scope of the invention and yielding the desired results when used in the process of the invention will include saturated aliphatic acids containing 12–18 carbon atoms. Either the individual acids or mixtures thereof may be used. Examples of these acids are stearic acid, palmitic acid, myristic acid, and lauric acid. Stearic acid is preferred since it is the one most readily available commercially in colorless form, and least expensive in such form. Other lubricants suitable for use in this invention include di- and tri-substituted esters of phosphoric acid with saturated aliphatic alcohols of from 12–18 carbon atoms, and mixtures thereof. Since the di-substituted esters are more easily prepared than the tri-, they will be preferred. Dilauryl phosphate is a desirable example.

The amounts of such lubricants to be used will ordinarily not exceed 2 parts per 100 parts of monomer. All proportions throughout the specification and claims are given by weight unless otherwise stated.

The present invention is broadly applicable to ethenoid monomers, either taken singly or in admixture, which ethenoid monomers give polymers adapted for use in plastics molding operations. Obviously, the invention assumes greatest importance with respect to those ethenoid compounds which are most advantageously used in the granular polymerization process although other ethenoid compounds which heretofore have been polymerized by other methods, may more advantageously be polymerized in water suspension in view of the benefits deriving from this invention.

Methyl methacrylate monomer is an ethenoid monomer, particularly adapted for use in the present invention and, likewise, mixtures of methyl methacrylate monomer with other monomers used in minor proportions, are well adapted for use in this invention. Other ethenoid monomers which may be used either alone or in admixture with each other or methyl methacrylate include vinyl acetate and other vinyl esters, styrene and its derivatives, and esters of acrylic and methacrylic acid and their derivatives.

There may be associated with the ethenoid monomer, at the start of the process, plasticizers selected and proportioned for their influence on the characteristics of the polymer which is to be made.

The amount of lubricant will be selected to meet the requirements of a given case as will be understood by those skilled in the art. For purposes of illustration only, the following may be stated as to the amounts to be used in parts per hundred parts of monomer:

With methyl methacrylate, unplasticized, the preferred amount is from 0.5 to 0.75 of one of the fatty acid lubricants or from 0.25 to 0.5 of one of the phosphate esters.

With plasticized methyl methacrylate, from 1.0 to 1.25 and from 0.75 to 1.0, respectively.

With the copolymer methyl methacrylate 90, styrene 10, from 1.0 to 1.25 and from 0.75 to 1.0, respectively.

With the copolymer methyl methacrylate 85, vinyl acetate 15, from 1.75 to 2.0 and from 1.25 to 1.5 respectively.

The general procedure of granulation polymerization, to which the present invention is applicable, is described in United States Patent 2,133,257 of D. E. Strain. In this procedure the monomeric liquid, either in admixture with plasticizer or not, has mixed with it a suitable proportion of a catalyst of polymerization, such as benzoyl peroxide, and is introduced into a larger volume of an inert liquid in which it is insoluble, ordinarily water, which serves as the vehicle. This vehicle has dissolved in it a sufficient quantity of a dispersing agent so that when the mixture is maintained under active agitation the monomeric liquid is maintained in the form of tiny droplets suspended in the vehicle. Polymerization is now effected by heating, preferably by the circulation of hot water through a jacket surrounding the container in which the batch has been mixed. A reflux condenser is attached to the container for the return of vaporized monomer and water. The reaction of polymerization is an exothermic one and it is ordinarily preferred to ensure the absorption of the excess heat by the provision of a generous circulation of water at the desired temperature in the jacket. This or other means of moderating the temperature of the batch is desirable, even though not essential, in connection with the present invention.

Under the preferred conditions described, the temperature of the mixture, as indicated by a thermometer immersed therein, remains substantially constant during the early stages of the reaction of polymerization. Subsequently, however, heat is produced by the reaction at a greater rate with the result that, in spite of the moderating influence of the water jacket, the temperature of the reaction batch rather suddenly rises, going within a few minutes to a peak value and then, immediately or very soon, decreasing again rather rapidly to or toward the initial level. The temperature then remains at the new level until polymerization has been substantially completed when the temperature again decreases to that of the surrounding water jacket.

For purposes of the present invention, the time during which the evolution of heat is at its maximum, which time may be very brief and is usually not more than a minute or two, will be referred to as the peak of the polymerization reaction, while the period during which occur the abrupt rise to the peak, the peak itself, and the rapid fall thereafter will be referred to as the peak period.

The abrupt rise of temperature marking the beginning of the peak period, and the level of temperature reached at the peak, can be moderated by temporarily increasing the rate of circulation of the cooling water, or by decreasing its temperature, but the fact that the characteristic rise in temperature may be obscured by such measures does not do away with the occurrence of the peak and does not reduce its significance in relation to the present invention. It is to be noted also that such partial suppression of the rise in temperature tends to lengthen the peak period.

The present invention is based upon the discovery that the objects are accomplished if any of the herein considered lubricants is added to the reaction batch within the peak period of the polymerization reaction and, preferably, as near the peak of the reaction as possible.

The postponement of the addition of the

mechanical difficulties which, as already described, have been observed when these lubricants are incorporated with the monomer at the beginning of the reaction of polymerization. These difficulties do not arise subsequently to the peak period.

It has been found by actual analysis that when the herein considered lubricants are added to the reaction batch during the peak period, and preferably at the peak itself, practically the entire amount thus added, which is of the order of two per cent or less of the weight of the initial monomer, is taken up by the material undergoing polymerization. Thus there are avoided the waste and uncertainty of lubricating effect which result if the lubricant is added after the completion of the polymerization.

There is also evidence, based upon suitable analytical procedure, that the lubricant is distributed almost entirely upon the surfaces of the globules, or at least that it penetrates the latter only very slightly. If the polymer is to be used in its globular granular form for molding, without an intermediate treatment upon mixing rolls or the like for the incorporation of auxiliary ingredients, it is evident that this location of the lubricant upon the surfaces of the granules is desirable in promoting an optimum of lubricating effect in the molds since it is only at the surfaces of such globules coming into contact with the metal of the molds that lubricating action is required.

This distribution of the lubricant upon the globules is different, however, from that which might be obtained by tumbling together a dry, unlubricated polymer with an equivalent amount of lubricant, as a means of causing the former to be coated by the latter. Polymer coated in this latter manner gives, when molded, a molded mass of granular character, i. e., one in which the shape of the granules from which it has been molded tends to persist in the form of a slight optical non-homogeneity. Articles molded from polymer lubricated in accordance with the present invention are not only free from these evidences of non-homogeneity but actually have a more limpid and brighter appearance than articles made from completely unlubricated polymer.

If it is desired to compound the granular polymer with auxiliary ingredients, particularly coloring ingredients, by kneading on mixing rolls, or in other suitable equipment, the polymer lubricated in accordance with the present invention is handled without difficulty. Having once been separated from the vehicle and dried, the granules weld together readily on hot rolls, yielding a continuous mass which does not drop from the rolls. The rolling operation is, accordingly, carried out as readily and as rapidly as though no lubricant were present.

The following examples are given to illustrate specific embodiments of the present invention:

Example I.—An aqueous vehicle is made up of:

	Parts
Distilled water	2000
$Na_2HPO_4.12H_2O$	0.5
$NaH_2PO_4.2H_2O$	0.5
Granulating agent	1.0

The granulating agent is a partially neutralized polymethacrylic acid and is furnished in dilute aqueous solution, the water content of which is included in the amount of water stated.

In a jacketed kettle equipped with agitator and reflux condenser there are introduced into this vehicle

	Parts
Methyl methacrylate monomer	1000
Benzoyl peroxide	4.0

While maintaining the jacket temperature at 86° C., the mixture is rapidly agitated. The monomer is thereby suspended in the form of tiny droplets in the vehicle.

In about 40 minutes the temperature of the mixture rises from that of reflux (about 83° C.) to about 88° C. to 91° C. At this point, there is added to the mixture:

	Parts
Stearic acid	5

in the form of a melted slurry in a little hot water.

Within a very few minutes after rising to a peak, the temperature falls gradually to about 86° C. Fifteen minutes after the occurrence of the peak, the circulation of hot water in the jacket is replaced by circulation of cold water. When the batch has thereby been cooled to about 35° C., the finely divided polymer is separated in a centrifuge, washed three times with distilled water, and then dried at 70° C. for about 24 hours.

This polymer can be molded by compression in an unlubricated mold and does not adhere to the mold. The molded article is transparent and brilliant, comparatively free of graininess, and not inferior in finish to the mold in which it is made.

Example II.—Into the aqueous vehicle of Example I is introduced a mixture of:

	Parts
Methyl methacrylate monomer	1000
Benzoyl peroxide	[illegible]

Polymerization is effected as in Example I. Immediately following the peak of the reaction there is added, suspended in a little hot water,

	Parts
Dilauryl phosphate	2.5

Subsequent procedure is as in Example I.

Example III.—Into the aqueous vehicle of Example I is introduced a mixture of:

	Parts
Methyl methacrylate monomer	900
Styrene monomer	100
Benzoyl peroxide	[illegible]

Polymerization is effected, by the application of heat, in a jacketed reflux kettle. At the peak of the reaction there is added:

	Parts
Stearic acid	10

The subsequent procedure is as in Example I.

Example IV.—The procedure of Example III was followed using a mixture of:

	Parts
Methyl methacrylate monomer	800
Methyl acrylate monomer	200

with

Benzoyl peroxide	10

as catalyst.

Example V.—The procedure of Example I is followed in the polymerization of a mixture of:

	Parts
Methyl methacrylate monomer	850
Vinyl acetate monomer	150

with

Benzoyl peroxide

as catalyst. At the peak of the reaction is added:

	Parts
Stearic acid	5

The dried polymer is compounded on hot rolls with:

	Parts
Cadmium yellow No. 4	4

and the resulting dough is cooled and ground.

Example VI.—The procedure of Example III was followed using a mixture of:

	Parts
Methyl methacrylate monomer	880
Vinyl acetate monomer	120
with	
Benzoyl peroxide	20

as catalyst, except that 10 parts of dimyristyl phosphate was used in place of the stearic acid as lubricant.

Example VII.—The procedure of Example III was again followed but using a mixture of:

	Parts
Methyl methacrylate monomer	900
Styrene monomer	100
with	
Benzoyl peroxide	20

as catalyst and using 5 parts of distearyl phosphate in place of the stearic acid as lubricant.

Example VIII.—Into the aqueous vehicle of Example I is introduced a mixture of:

	Parts
Methyl methacrylate monomer	900
Diamyl phthalate (plasticizer)	100
Benzoyl peroxide	1.1

Polymerization of the monomer is effected in the manner described in Example I. Immediately following the occurrence of the peak of the reaction there is added, in molten condition, suspended in a little hot water,

	Parts
Palmitic acid	20

The balance of the procedure is as in Example I.

Example IX.—The procedure of Example I is carried out except that the amount of stearic acid added is 20 grams.

Following the drying, the resulting lubricated polymer is compounded on hot mixing rolls with dibutyl phthalate, 110 parts, and the resulting dough is cooled and ground.

Example X.—The procedure of Example III was followed using a mixture of:

	Parts
Methyl methacrylate monomer	850
Diamyl phthalate (plasticizer)	150
with Benzoyl peroxide	8

as catalyst, except that 14 parts of myristic acid was used in place of the stearic acid as lubricant.

It will be understood that the above examples are merely illustrative and that the invention is applicable to the ethenoid monomers adapted for use in plastics molding procedures whether used alone or in admixture. The coloring matter, plasticizer, and catalyst specified in the examples, as well as modifiers generally, may be replaced with others without any particular regard to the present invention.

The present invention provides a simple and inexpensive procedure for the addition of lubricant in the course of the manufacture of polymethyl methacrylate and the like. It involves no complications in operating procedure and in many cases eliminates the necessity of a kneading operation, thereby reducing operating cost. The resulting products are effectively lubricated for molding and are not injured in any respect by the presence of the lubricating substance. On the contrary, the invention tends to improve the quality of the molded articles, as regards homogeneity and clearness.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. In the granular polymerization of an ethenoid monomer from the group consisting of vinyl esters, styrene, and esters of acrylic and methacrylic acids, the steps comprising dispersing said ethenoid monomer in water containing a dispersing agent, initiating polymerization of said monomer, and adding to said dispersion during the peak period of the evolution of heat by the polymerization reaction a lubricant of acidic character from the group consisting of the saturated aliphatic acids containing 12–18 carbon atoms, inclusive.

2. In the granular polymerization of an ethenoid monomer from the group consisting of vinyl esters, styrene, and esters of acrylic and methacrylic acids, the steps comprising dispersing said ethenoid monomer in water containing a dispersing agent, initiating polymerization of said monomer, and adding to said dispersion during the peak period of the evolution of heat by the polymerization reaction up to 2.0 parts, per 100 parts of said monomer, of a lubricant of acidic characted from the group consisting of the saturated aliphatic acids containing 12–18 carbon atoms, inclusive.

3. In the granular polymerization of methyl methacrylate monomer, the steps comprising dispersing said methyl methacrylate monomer in water containing a dispersing agent, initiating polymerization of said monomer, and adding to said dispersion during the peak period of the evolution of heat by the polymerization reaction a lubricant of acidic character from the group consisting of the saturated aliphatic acids containing 12–18 carbon atoms, inclusive.

4. In the granular polymerization of methyl methacrylate monomer, the steps comprising dispersing said methyl methacrylate monomer in water containing a dispersing agent, initiating polymerization of said monomer, and adding to said dispersion during the peak period of the evolution of heat by the polymerization reaction up to 2.0 parts, per 100 parts of said monomer, of a lubricant of acidic character from the group consisting of the aliphatic acids containing 12–18 carbon atoms, inclusive.

5. In the granular polymerization of a mixture of ethenoid monomers from the group consisting of vinyl esters, styrene, and esters of acrylic and methacrylic acids, of which mixture at least a major portion is methyl methacrylate, the steps dispersing said mixture of ethenoid monomers in water containing a dispersing agent, initiating polymerization of said monomers, and adding to said dispersion during the peak period of the evolution of heat by the polymerization reaction a lubricant of acidic character from the group consisting of the saturated aliphatic acids containing 12–18 carbon atoms, inclusive.

6. In the granular polymerization of a mixture of ethenoid monomers from the group consisting of vinyl esters

methacrylic acids, of which mixture at least a major portion is methyl methacrylate, the steps dispersing said mixture of ethenoid monomers in water containing a dispersing agent, initiating polymerization of said monomers, and adding to said dispersion during the peak period of the evolution of heat by the polymerization reaction up to 2.0 parts, per 100 parts of said mixture of monomers, of a lubricant of acidic character from the group consisting of the saturated aliphatic acids containing 12–18 carbon atoms, inclusive.

7. In the granular polymerization of a mixture of ethenoid monomers from the group consisting of vinyl esters, styrene, and esters of acrylic and methacrylic acids, of which mixture at least a major portion is methyl methacrylate, the steps comprising dispersing said mixture of ethenoid monomers in water containing a dispersing agent, initiating polymerization of said monomers, and adding to said dispersion during the peak period of the evolution of heat by the polymerization reaction stearic acid as a lubricant.

DAVID A. FLETCHER.

be of such small diameter that the material has a powder-like appearance in bulk. This granular product is particularly easy to remove from the polymerisation vessel and after washing and drying may be applied directly for any purpose for which the polymer is commonly employed without the necessity of previous grinding, cutting or other comminuting treatment.

If desired, a proportion of plasticiser substantially insoluble in water may be mixed with the unsaturated ester before commencing the polymerisation, and a plasticised granular polymer will thus be obtained. Similarly, dyed, tinted or filled polymer may be produced if desired.

The invention is illustrated by the following examples in which all the parts are by weight.

EXAMPLE 1.

100 parts of methyl methacrylate were mixed with 200 parts of water containing in solution 4 parts of poly-sodium methacrylate. The mixture was stirred at 1000 r.p.m. by a propeller stirrer and steam was blown in until the temperature reached 80° C. This temperature was then maintained by cutting down the steam supply. After 40 minutes the temperature began to rise and steam was shut off. When a maximum temperature of 87° C. was reached the stirred mixture was cooled to 60° C. by the addition of cold water. The spherical granules were separated by centrifuging, washed with water at 70° C. centrifuged and dried in trays for one hour at 100° C.

EXAMPLE 2.

100 parts of methyl methacrylate containing in solution 1 part of benzoyl peroxide were mixed with 2000 parts of water containing in solution 20 parts of poly-sodium methacrylate. The mixture was stirred at 300 r.p.m. by a gate stirrer and treated as described in Example 1.

EXAMPLE 3.

100 parts of methyl methacrylate containing in solution one part of benzoyl peroxide were mixed with 200 parts of water containing in solution 5 parts of caustic soda. The mixture was stirred at 600 r.p.m. by a propeller stirrer and treated as described in Example 1.

EXAMPLE 4.

100 parts of methyl methacrylate containing in solution 1 part of benzoyl peroxide mixed with 500 parts of water containing 5 parts of polymethacrylamide were stirred at 1500 r.p.m. with a propeller stirrer and treated as in Example 1.

Dated the 17th day of September, 1934.

E. C. G. CLARKE,
Imperial Chemical House, Millbank,
London, S.W.1.
Solicitor for the Applicants.

COMPLETE SPECIFICATION

Improvements in or relating to Plastic Materials and to Methods of Production thereof

We, ARCHIBALD RENFREW, JAMES MARTIN WALTER, and WILLIAM ELLIOTT FREW GATES, all British subjects, all of Norton Hall, The Green, Norton-on-Tees, County Durham, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the production of plastic materials by the polymerisation of vinyl esters or the lower alkyl esters of acrylic acid, methacrylic acid or other homologues of acrylic acid, or mixtures of such esters.

It has already been proposed to conduct the polymerisation of derivatives of acrylic acid, or their homologues, or vinyl esters, or their homologues, by emulsifying such derivatives in liquids in which they are substantially insoluble, and subsequently polymerising the said derivatives. In one such previous proposal the emulsions were preferably prepared with the aid of an emulsifying and/or wetting agent, and in certain specific modifications of this process the emulsions were described as being stirred during the polymerisation step. The products obtained in this process varied from latex-like liquids to solids, and when treating acrylic nitrile either alone or in admixture with other polymerisable substances, the product was sometimes obtained in granular form. The treatment, however of esters such as ethyl acrylate resulted in all cases in a latex-like product which required coagulation with acid in order to recover the solid product which was then obtained as a rubbery mass.

In British Patent No. 427,494 is described the production of granular or or globular polymerisation products by carrying out the polymerisation in the presence of an aqueous solution of certain cellulose derivatives or carbohydrates which have the property of hindering coalescence of the polymerising droplets without forming substantial amounts of a stable emulsion.

We have now discovered an improved method for carrying out the polymerisation of vinyl esters or the lower alkyl esters of acrylic acid or its homologues or mixtures of such esters in such a manner that about 90—99% of the monomeric ester is converted into the form of smooth spherical or lentil shaped granules. The spherical granules vary in size from about 0.001" to about 0.1".

According to our invention the monomeric ester is polymerised in admixture with water which contains in solution from about 0.1 to about 10% of a polyvinyl alcohol, an amide of polyacrylic acid or its homologues, a metallic salt of polyacrylic acid or its homologues, or mixtures of the same, the mixture being continually stirred during the polymerisation. Preferably the weight of added aqueous solution should be not less than about equal to the weight of monomeric ester to be polymerised.

It is sometimes possible to form the polymeric water-soluble body in situ, e.g. the presence of about 2% NaOH to about 10% NaOH (calculated on the water present) in the stirred and heated mixture of one part methyl methacrylate with two parts water, causes the formation of sodium methacrylate which polymerises to give poly-sodium methacrylate.

When heat is used for effecting polymerisation, any temperatures up to that at which the mixture or any component thereof refluxes may be employed. Any desired pressure at below or above atmospheric may be maintained in the polymerisation vessel. Polymerisation catalysts such as benzoyl peroxide, hydrogen peroxide or benzaldehyde may be present.

It is characteristic of our invention that agitation is essential from the inception of the actual polymerisation until the product is quite solid, since the medium is of such a type that separation into two liquid phases takes place if the agitation is interrupted before or shortly after the inception of polymerisation, while coalescence of the partly polymerised particles into an unwieldy mass takes place if agitation is discontinued before the particles have become sufficiently solid.

Polymerised material produced by the process of the present invention is in the form of solid granules which are chemically and physically homogeneous although the granules may or may not be of such small diameter that the material has a powder-like appearance in bulk. This granular product is particularly easy to remove from the polymerisation vessel and after washing and drying may be applied directly for any purpose for which the polymer is commonly employed without the necessity of previous grinding, cutting or other comminuting treatment.

If desired, a proportion of plasticiser substantially insoluble in water may be mixed with unsaturated ester before commencing the polymerisation, and a plasticised granular polymer will thus be obtained. Similarly, dyed, tinted or filled polymer may be produced if desired. Such added substances may be conveniently described in general as "modifying agents".

The invention is illustrated by the following examples in which all the parts are by weight.

EXAMPLE 1.

100 parts of methyl methacrylate were mixed with 200 parts of water containing in solution 4 parts of poly-sodium methacrylate. The mixture was stirred at 1000 r.p.m. by a propeller stirrer and steam was blown in until the temperature reached 80° C. This temperature was then maintained by cutting down the steam supply. After 40 minutes the temperature began to rise and steam was shut off. When a maximum temperature of 85° C. was reached the stirred mixture was cooled to 60° C. by the addition of cold water. The spherical granules were separated by centrifuging, washed with water at 70° C. centrifuged and dried in trays for one hour at 100° C.

EXAMPLE 2.

100 parts of methyl methacrylate containing in solution 1 part of benzoyl peroxide were mixed with 2000 parts of water containing in solution 20 parts of poly-sodium methacrylate. The mixture was stirred at 300 r.p.m. by a gate stirrer and treated as described in Example 1.

EXAMPLE 3.

100 parts of methyl methacrylate containing in solution one part of benzoyl peroxide were mixed with 300 parts of water containing in solution 5 parts of caustic soda. The mixture was stirred at 600 r.p.m. by a propeller stirrer and treated as described in Example 1.

EXAMPLE 4.

100 parts of methyl methacrylate containing in solution 1 part of benzoyl peroxide were mixed with 500 parts of water containing 5 parts of polymethacrylamide were stirred at 1500 r.p.m. with a propeller stirrer and treated as in

Example 1.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the production of granular or globular polymerisation products of vinyl esters, or of the lower alkyl esters of acrylic acid or its homologues, or of mixtures of such esters, with or without the addition of known modifying agents, which comprises polymerising the ester or esters in the presence of a water layer containing in solution approximately 0.1 to 10% of a polyvinyl alcohol an amide of polyacrylic acid or its homologues, or mixtures of the same, the two liquid phases being intermingled by stirring continuously during the polymerisation.

2. Process for the production of granular or globular polymerisation products of methyl methacrylate with or without the addition of known modifying agents, which comprises polymerising the ester in admixture with water containing in solution approximately 0.1 to 10% of polymeric sodium methacrylate, the mixture being stirred continuously during the polymerisation.

3. Process as claimed in Claim 2, in which the polymeric sodium methacrylate is prepared in situ by heating the mixture of ester and water in the presence of caustic soda.

4. Process for the production of granular or globular polymerisation products substantially as described and illustrated with reference to the foregoing examples.

5. Granular or globular polymerisation products whenever prepared by the methods claimed in any of the preceding claims.

Dated the 12th day of September, 1935.

E. C. G. CLARKE,
Imperial Chemical House, Millbank,
London, S.W.1,
Solicitor for the Applicants.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1936.

temperature between 125° C. and 135° C. so that the product distilled at a steady rate. On completion of the addition steam was admitted to the flask in order to steam distil out the last traces of ester remaining, the distillate during this stage being combined with that from the previous stage.

The total product separated into two layers consisting of (a) an upper layer (1338 parts) containing 82.1% of methyl methacrylate and (b) a lower aqueous layer (500 parts) containing 30% of methanol and traces of ester. The yield of methyl methacrylate obtained in the upper layer was 7[illegible]% calculated on the amount of acetone cyanhydrin used.

Dated the 28th day of October, 1937.

E. A. BINGEN,
Solicitor for the Applicants.

COMPLETE SPECIFICATION

Improvements in or relating to the Manufacture of Methacrylic Acid Esters

We, George Edwin Wainwright, of Norton Hall, The Green, Norton-on-Tees, Durham, and Joseph Horsefield Brown, of Norton Hall, The Green, Norton-on-Tees, Durham, both British Subjects, and Imperial Chemical Industries Limited, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to an improved process for the manufacture of methacrylates, and particularly to the manufacture of the lower alkyl methacrylates such as methyl methacrylate.

The manufacture of methacrylic acid esters of monohydric alcohols by reacting acetone cyanhydrin with concentrated or fuming sulphuric acid at a raised temperature, and subsequently heating the reaction mixture with an appropriate alcohol with or without added water, has been described in Specifications Nos. 405,699 and 427,810.

In Specification No. 456,683 there is described a method of reacting acetone cyanhydrin with sulphuric acid in which the mixture of the reactants is heated to a temperature of 140—180° C. for a time not substantially greater than 10 minutes.

According to the present invention methacrylic acid esters are prepared by slowly adding to the reaction product of acetone cyanhydrin and sulphuric acid, both water and an alcohol of the type ROH (where R is a lower alkyl radical containing not more than four carbon atoms) while maintaining an elevated temperature such that esterification and the distillation of the resulting ester proceed simultaneously. Preferably the ester is distilled off through a fractionating column.

When operating in this manner the ester is obtained more quickly, the time required to esterify a given quantity of alcohol being decreased in many cases by as much as a half. We also find that better yields of the ester can be obtained than by known processes.

In Specifications Nos. 405,699 and 427,810 the preferred proportions of the reactants to be used in the preparation of methacrylates are disclosed. In the process according to the present invention the amount of alcohol to be added to the acetone cyanhydrin-sulphuric acid mixture is not modified by adopting the variation in procedure, and in general it may be stated that amounts between 1 mol. and 2 mols. per mol. of acetone cyanhydrin are satisfactory, though to obtain the maximum yields not less than 1.5 mols. should be used. The amount of water should not exceed 4 mols. per mol. of cyanhydrin nor be less than 0.5 mol., quantities of the order of 2 mols. being satisfactory. In the case of the alcohols miscible with water the water and the alcohol are most satisfactorily added as a mixture in the chosen proportions. The rate of addition of the mixture does not appear critical and we have obtained satisfactory results using such rates that between half an hour and three hours are required to add all the mixture. In general, rates giving an addition time of two hours are preferable. When higher alcohols which are not miscible with water are used in the process of the invention separate feeds for water and alcohol are required.

The process may be carried out at either ordinary or reduced pressures, e.g. half an atmosphere, and the temperature during the water-alcohol addition should be such that distillation proceeds steadily at the prevailing pressure. When preparing the propyl and butyl esters at atmospheric pressures, temperatures between 130° and 160° C. are convenient; with the methyl ester temperatures of 100—120° C. suffice, though temperatures up to e.g.

little ester, the remainder being water. The yield of ethyl methacrylate in the upper layer was 67% calculated on the acetone cyanhydrin used.

EXAMPLE 3.

Butyl methacrylate was made by the procedure of Example 2 the mixture of water and ethyl alcohol being replaced by water (180 parts) and butyl alcohol (555 parts) fed simultaneously from separate vessels, and the temperature during distillation being maintained between 130 and 155° C. The yield of butyl methacrylate calculated on the acetone cyanhydrin used was 62%.

EXAMPLE 4.

Butyl methacrylate was prepared as in Example 3 the pressure being maintained during the reaction between ½ and ⅔ of atmospheric, while the temperature was kept at 120—130° C. The yield was 68% calculated on the acetone cyanhydrin used.

EXAMPLE 5.

Acetone cyanhydrin (12.7 parts 95% pure) was added to sulphuric acid (22 parts) containing copper, while maintaining the temperature below 90° C. The mixture was then heated for 1 hour at 130° C. when a mixture of methanol (9.6 parts) and water (5.4 parts) containing hydroquinone was run in over a period of two hours while the product was allowed to distil through a fractionating column. The temperature during this process was 128—130° C. At the end of the addition residual ester was steam distilled from the reaction vessel. The total distillate (22 parts) was treated with a saturated solution (21 parts) of common salt when an upper layer (12.1 parts) was formed containing 94% methyl methacrylate. The lower brine layer was discarded. The ester present in the upper layer represents a yield of 80% on the acetone cyanhydrin used.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the manufacture of methacrylic acid esters which comprises slowly adding to the reaction product of acetone cyanhydrin and sulphuric acid both water and an alcohol of the type ROH (where R is a lower alkyl radical containing not more than four carbon atoms) while maintaining an elevated temperature such that esterification and the distillation of the resulting ester proceed simultaneously.

2. Process as claimed in Claim 1 in which the reaction with water and alcohol is carried out at reduced pressure.

3. Process as claimed in Claim 1 in which the removal of the resulting ester is completed by steam distillation.

4. Process as claimed in Claims 1, 2 or 3 in which the heating is carried out in the presence of an antipolymerisation material such as tannic acid, sulphur, hydroquinone or freshly precipitated copper.

5. Process for the manufacture of methacrylic acid esters substantially as hereinbefore described.

6. Methacrylic acid esters whenever prepared by the methods claimed in any of the preceding claims.

Dated the 28th day of October, 1938.
E. A. BINGEN,
Solicitor for the Applicants.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1939.

150° C. may be used. With pressures of about half an atmosphere the temperature limit for the propyl and butyl esters may also be extended down to approximately 100° C. Temperatures much above 160° are to be avoided, since polymerisation may ensue and also side reactions leading to the formation of unwanted products. We may minimise the tendency for polymerisation to occur by having present during the heating an antipolymerisation material such as tannic acid, sulphur, hydroquinone or freshly precipitated copper.

The usual method of reacting acetone cyanhydrin with sulphuric acid as the first stage in the formation of methacrylic acid esters involves heating a mixture of the two to temperatures in the neighbourhood of 140° C. and when it is proposed to perform the esterification step immediately afterwards it is convenient to add the water and alcohol to the hot reaction mixture. It is then not necessary to apply heat during the initial period of the alcohol-water addition, though it is subsequently necessary in order to maintain the reaction vessel at such a temperature that the ester distils over.

When the whole of the alcohol and water has been added a continued heating for a short time only, suffices to recover substantially all the product, although it is advisable for maximum yields to subject the residue in the reaction vessel to a short period of steam distillation. In many cases the reaction mixture may be steam distilled directly all the alcohol has been added with very satisfactory results. The ester distilling off through the fractionating column is condensed together with water, alcohol and a little acid which may pass through the column. If allowed to stand this product separates into two layers, the upper one being the larger and consisting chiefly of ester together with a small proportion of water, unchanged alcohol and methacrylic acid, while the lower layer consists chiefly of water together with unchanged alcohol amounting to 20—30% of the lower layer and a small proportion of ester. The two layers can then be separated and the upper one worked up to give pure ester, while the lower one may be rejected, or it may be mixed with more alcohol and used to treat a further quantity of the acetone cyanhydrin-sulphuric acid reaction product. By adopting this recycling of the lower layer, its ester content can be recovered in a simple manner and its alcohol content converted to ester. In another method of working up the product where the lower layer is not to be returned to the reaction mixture, the whole of the distillate may be washed with brine and the aqueous layer allowed to settle out and then removed. In this way loss of ester in the aqueous layer is minimized.

The following Examples illustrate but do not limit our invention, all parts being by weight.

EXAMPLE 1.

Acetone cyanhydrin (1275 parts 95% pure) was mixed with sulphuric acid containing 2% SO_3 (2175 parts) and copper (5 parts) at a temperature of 80° C. and then heated to a temperature of 150° C. for a period of 5 minutes. To the reaction mixture was then added a mixture of water (540 parts) and methanol (720 parts) containing hydroquinone (2.5 parts) at a uniform rate over a period of 2 hours, and vapour evolved from the reaction mixture during the addition was removed through a 5-plate fractionating column, condensed and collected. During this stage the reaction mixture was maintained at a temperature between 125° C. and 135° C. so that the product distilled at a steady rate. On completion of the addition steam was admitted to the flask in order to steam distil out the last traces of ester remaining, the distillate during this stage being combined with that from the previous stage.

The total product separated into two layers consisting of (a) an upper layer (1838 parts) containing 82.1% of methyl methacrylate and (b) a lower aqueous layer (600 parts) containing 30% methanol and traces of ester. The yield of methyl methacrylate obtained in the upper layer was 77% calculated on the amount of acetone cyanhydrin used.

EXAMPLE 2.

Acetone cyanhydrin (425 parts 95% pure) was mixed with sulphuric acid (725 parts) and copper (2 parts) at a temperature of 85° C. and then heated to 125—130° C. for approximately 1½ hours. To the hot reaction mixture was then added a mixture of water (180 parts) and ethyl alcohol (345 parts) containing hydroquinone (5 parts) at a uniform rate over a period of an hour; the temperature at first rose to 148° C. and then began to fall. Heating was then commenced to maintain the temperature at 130—150° C. allowing the product to distil off through a fractionation column; when all the water-alcohol mixture had been added the ester remaining in the vessel was removed by steam distillation.

The total product separated into two layers consisting of (a) an upper layer (549 parts) containing 67% of ethyl methacrylate and (b) a lower layer (176 parts) containing 30% of ethyl alcohol and a

65-4397

Ex 12D

SAC, Philadelphia 7/10/50

SA T. SCOTT MILLER, JR.

HARRY GOLD, was.
ESPIONAGE - R

EXHIBIT 65-4307-1B-13 (1) (Exhibit 12D)

On 6/25/50, GOLD examined the material contained in the above folder, at which time he stated that the written material was in his handwriting and consisted of notes on work in connection with the synthesis of dimethyl hexine diol, which work he did in May of 1947, according to the notes. The remainder of the material is technical equipment literature. In connection with the folder on HENDRICK mixing equipment, GOLD stated that there were two possibilities as to why he had this in his possession: (1) The material was obtained from BROTHMAN's files and was accidentally mixed in with material which GOLD was interested in when he left BROTHMAN's employ. GOLD added that he would have very little use for something of this nature. (2) BROTHMAN had given him this folder for GOLD to submit to the Soviet Union, which GOLD never did. GOLD said the first possibility was the more likely.

EXHIBIT 65-4307-1B-13 (1) (Exhibit 12H)

On the same date GOLD examined the material in this folder and gave the following explanations:

The letter dated 2/21/47 to BROTHMAN on the stationery of PENNIE, EDMONDS, MORTON & BARROWS was in connection with patents which related to processes on which the BROTHMAN firm was working. GOLD stated that he recalled BROTHMAN dealt with ARNOLD R. WORKMAN, an attorney who is listed as an associate of the firm.

Relative to the letter from the AMERICAN CYANAMID COMPANY, dated 1/7/47, this was in connection with the manufacture of acetone.

The three pages dated 12/12/46 and entitled "Seminar," GOLD stated, were notes taken at a seminar held in BROTHMAN's office. BROTHMAN started having these seminars to acquaint members of the organization who were not familiar with chemistry, etc., with the general theory in those fields. GOLD said these seminars never got beyond the chemical field as BROTHMAN finally came to the conclusion they were too time consuming.

EXHIBIT 65-4307-1B-13 (1) (Exhibit 12I)

On the same date GOLD examined the material in the above folder, at which time he stated that the majority of the handwriting was his own and that the work

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was done in connection with GOLD's employment by BROTHMAN. GOLD identified this material as notes and work on the methyl methacrylate molding powder; the snythesis of B-complex vitamins in connection with a report being prepared for AMTORG TRADING CORPORATION in 1946; and the small 8" x 5" pieces of paper indicate research done on the alternate synthesis of nylon, which was connected with BROTHMAN's office and was not part of the data on nylon obtained by SLACK from HOWARD GOCHENAUR of the DUPONT COMPANY in Belle, West Virginia. Also contained in this folder are schedules of work to be done at the BROTHMAN laboratory. GOLD recognized that some of the handwriting on the material in this folder is that of SOL FANSHEL.

EXHIBIT 65-4307-1B-13 (1) (Exhibit 12J)

On the same date GOLD examined the material in the above folder, at which time he said that all this material consisted of laboratory notes, calculations, laboratory reports, etc., in connection with work being done by the BROTHMAN firm in late 1946 and early 1947. GOLD said he recognized his own handwriting as well as that of BILL ROHOLL, SY SILVERSTEIN, and BROTHMAN.

EXHIBIT 65-4307-1B-13 (1) (Exhibit 12K)

On the same date, after examining the material in the above folder, GOLD stated that all of the material in this folder, with the exception of the last page, dealt with a scheme for writing a patent on the methyl methacrylate synthesis and an ozonalysis process in connection with the work on methyl methacrylate. GOLD stated that in connection with the ozonalysis notes, he thought that he made them while conducting experiments in the laboratories of the OZONE PROCESSES COMPANY in Philadelphia, at a time when BROTHMAN was considering the purchase of an ozonizer to be used in research being conducted by the BROTHMAN firm at that time. GOLD said he made several trips to Philadelphia for the purpose of conducting these experiments, but that an ozonizer was not purchased.

GOLD stated that the last page of notes, which is on ruled paper, consist of rough draft notes in connection with the building of the plant for the STANTON LABORATORIES.

EXHIBIT 65-4307-1B-13 (1) (Exhibit 12L)

On the same date GOLD examined the material in this folder and gave the following observations:

Most of this material, according to GOLD, consists of laboratory notes of BROTHMAN in connection with the methyl methacrylate synthesis, material GOLD was to look up in the library, and GOLD's instructions to people in the laboratory relative to experiments. GOLD also stated that there are a list of material to be ordered in connection with the STANTON job, patent numbers, and notes on the diol synthesis.

One piece of paper, which is marked "#1" in red by the writer, has, among other notations, the following: "Rochester and Buffab - Lincoln Terr. - Kelly Mem. - Avenue S and E. 14 - SO 8-2300 - CL 3-4600 - GR 3-8604." GOLD stated that he thought these notations were in the handwriting of SY SILVERSTEIN, who was employed by BROTHMAN, and he thought that these notes identified firms or individuals from whom material and chemicals were ordered by the BROTHMAN firm.

EXHIBIT 65-4307-1B-13 (1) (Exhibit 12M)

On the same date GOLD identified the three pages of notes in this folder as being notes he took on 3/10/48 while he was conducting an experiment in the laboratory of the OZONE PROCESSES COMPANY in Philadelphia, on the dimethyl hexine diol process. GOLD said that this was in connection with the experiments to determine if the BROTHMAN firm had use for an ozonizer.

EXHIBIT 65-4307-1B-13 (1) (Exhibit 12N)

On the same date GOLD examined the material in the instant folder and stated that with the exception of the group dated 4/9/46, the material consisted of his own calculations and BILL ROHDLL's notes on processes being worked on by the BROTHMAN laboratory.

Relative to the material dated 4/9/46 and marked "#1" in red by the writer, GOLD said that this material was in the handwriting of BILL ROHDLL and concerned the work on a production process of pentaethyl tetranitrate. GOLD said that this was an explosive which BROTHMAN made in his laboratory and which BROTHMAN commenced working on prior to the time that GOLD entered the employ of BROTHMAN. GOLD said BROTHMAN was working on this production of "PETN." (pentaethyl tetranitrate) so that it could be made in a plant in Palestine with the same equipment used in DDT, on which BROTHMAN was also working. GOLD said that BROTHMAN told him that the idea was to build plants in Palestine which produce a peacetime product such as DDT, but which could also be used to immediately produce a wartime product such as "PETN."

GOLD said that BROTHMAN was involved in this work of designing plants which would have a dual purpose, as described above, with an individual by the name of ELIA SHALLIT and a man by the name of SLOVAN. GOLD said he thought that it was for this purpose that the PALESTINIAN POTASH COMPANY was formed.

GOLD said that BROTHMAN had a quarrel with SLOVAN in about August of 1946 and told SLOVAN that he was too busy on other work to continue his work with SLOVAN and SHALLIT.

EXHIBIT 65-4307-1B-13 (1) (Exhibit 12O)

On the same date GOLD examined the material in this folder, at which time he stated that this appeared to be notes of ROLFE WOLLAN in connection with the work on the molding of methyl methacrylate, which work, as shown by these notes, was done prior to the time GOLD was employed by the BROTHMAN firm. GOLD said that some of the notes are in BROTHMAN's handwriting.

EXHIBIT 65-4307-1B-13 (1) (Exhibit 12P)

On the same date GOLD identified all of the material in the above folder as being his own notes in connection with work on chlorine products for the METTUR CHEMICAL COMPANY, and notes dated 4/3/47 in connection with the work on a new vanishing cream on which the BROTHMAN firm was working for JULIAN BRODIE.

EXHIBIT 65-4307-1B-13 (1) (Exhibit 12R)

On the same date GOLD identified all the notes in this folder as being in his handwriting and pertaining to work on solvents. GOLD stated there was a possibility that these might be notes of his when tutoring someone in chemistry at one of his places of employment, either PENNSYLVANIA SUGAR or ABRAHAM BROTHMAN.

EXHIBIT 65-4307-1B-13 (1) (Exhibit 12S)

On the same date this folder, which was entitled "Notes from DOC," in GOLD's handprinting, was shown to him, at which time GOLD stated that the material consisted of notes of Dr. GUSTAV REICH, who was GOLD's superior at the PENNSYLVANIA SUGAR COMPANY. GOLD said there were also some notes in the handwriting of himself and MORRELL E. DOUGHERTY on their work at the PENNSYLVANIA SUGAR COMPANY.

EXHIBIT 65-4307-1B-13 (1) (Exhibit 12T)

On the same date the above folder, labelled in GOLD's handprinting, "CO 2 Recovery," was shown to GOLD, at which time he stated that all of this material consisted of notes, etc. he had made in connection with work for Dr. REICH at PENNSYLVANIA SUGAR in 1941, on Dr. REICH's CO 2 recovery process. GOLD stated that he also saw some of Dr. REICH's handwriting in the material and, further, that some of the work was done in 1938.

EXHIBIT 65-4307-1B-13 (1) (Exhibit 120)

On the same date GOLD examined the material in the above folder, at which time he said that the white pieces of paper contain his handwriting and are concerned with his work for Dr. REICH on the CO 2 recovery process. GOLD stated that his handwritten notes on the yellow pieces of paper are his tutoring notes in organic chemistry.

AmOH - [illegible] 5-8-47

(attempted formation of AmOK)

Charge
150 cc AmOH
66 gm. KOH (85%)
{ 3 gm. methylal
[illegible] C6H6
17.7 gm. Me2CO

Dehydration
382.1 Tare + 150 cc AmOH
260.0 tare
122.1 gm. AmOH

382.1 tare + AmOH
66.0 gm. KOH
448.1 gm. tare + AmOH + KOH

[illegible]	Lower Col	Vapor	Distillate H2O	Distillate AmOH	V[illegible]
65	124	91	—	—	60
71	132	93	5	10	60
00	139 (?)	91	11	18	65
207	132	92	12	21	70
216	139	110½	13	31	70/68
28	148	~~99~~ 105	13½	43	71
34	154	109			74
40	155	118	14	56	74
66	Stopped — material in flask very viscous, vapors not condensed				
—	—	—	15	71	74

added 75 cc (methanol → + 50 C 8 $\frac{50}{PM}$

agitated ½ hr 8 $\frac{20}{PM}$ @ 13°C

passed in C_2H_2 for 20 min 8 $\frac{22}{}$ @ 0°C ([illegible])

allowed to rise to 13°C 9 $\frac{10}{PM}$

added 197 gms. Me_2CO — went to solid gel at 9 $\frac{40}{}$
(C_2H_2 passed in all the while)

Reacted for 2 hrs. @ 13-15°C — 11 $\frac{40}{PM}$

decomposed with 150 cc No 14 — 1 $\frac{20}{PM}$

and at 2-5°C. held overnight. pH ~~6.3~~

distillation 5-9-47.

T Pot	Lower Col	Vapor	Press	Notes
				pH 6.9
0	—	—	100 —	[illegible]
-5	—	—	100 —	
0	—	—	100 —	pH 6.9 adj to 6.3
				[illegible]
35	30	29	60	
73	50	38	50	
95	76	67	50	
95	78	74		
9.5	~~65~~	57	30	

yield 22.0 gms. [illegible]
crude - approx 75%

[illegible] Test 3 g/g. Am OH → fair
possibly 2-3%

amOH – Heptane run

Charge
- 66 gms. KOH (85%)
- 150 cc n-AmOH
- 143 gms CaC2
- C2H2 ?

Dehydration

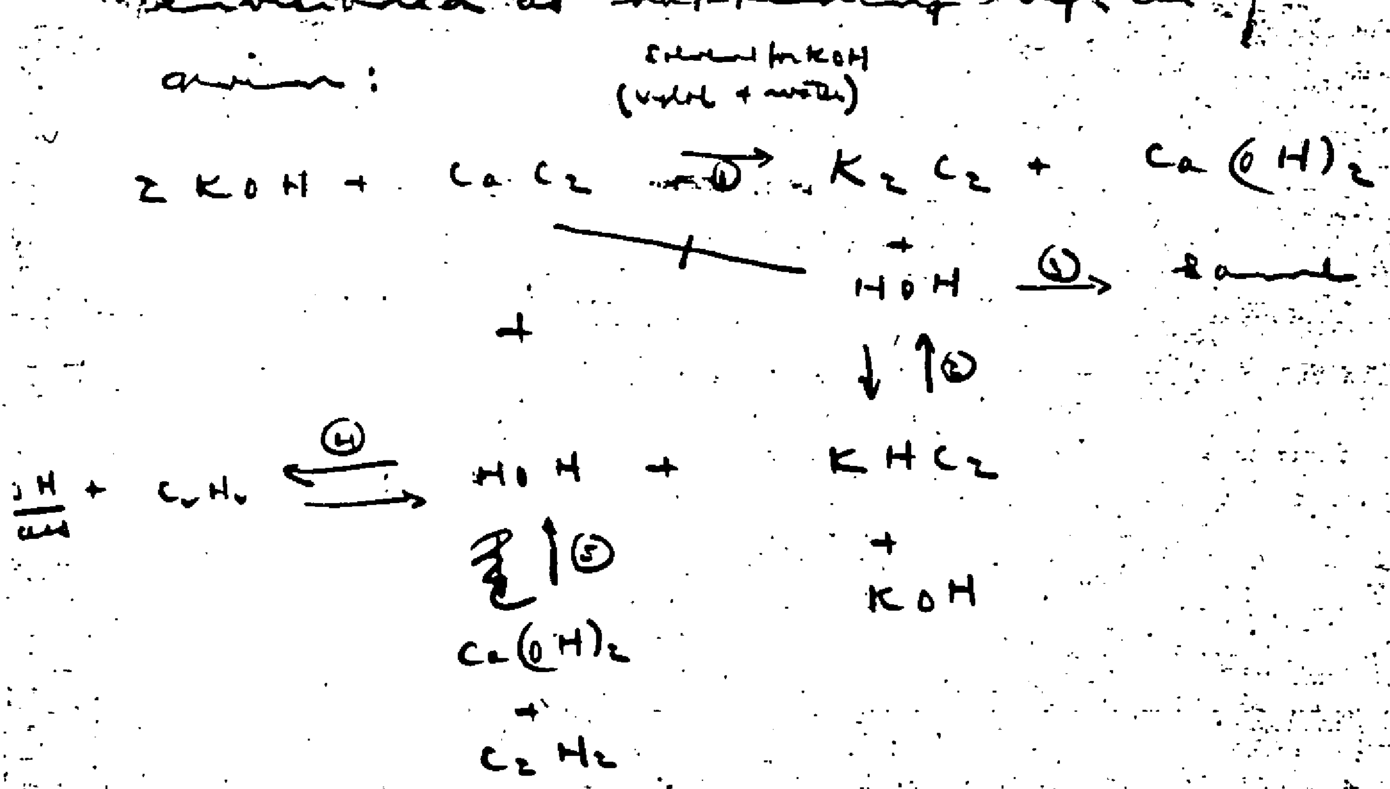
391.6 tare + AmOH
266.6 tare
125.0 gms. AmOH
66.0 gms. KOH
391.6 tare + AmOH
457.6

	Flask	Lower col	Vapor	Distillate H2O	Distillate AmOH
	161	114	88	0	0
	168	128	91	2	10 (?)
5	176	129	92	4	10
5	180	131	93	5	11
5	183	132	94	6	14
5	187	133	95	8	16
75	190	133	92	9	16
77	196	134	206	10	20
78	210	138	101	11	31
80	215	139	119	12	32

Theory

In order to obtain as quantitative as possible a yield of acetylenic glycol ~~some~~ postulate the following conditions:

1. The reaction between KOH and CaC_2 must be set so that substantially only K_2C_2 and KHC_2 are produced.
2. The production of the K_2C_2 and KHC_2 is envisioned as happening thru the following scheme:



a- reactions ①, ②, and ⑤ are irreversible

AMERICAN CYANAMID COMPANY
30 ROCKEFELLER PLAZA
NEW YORK 20, N.Y.

CABLE ADDRESS LIMENITRO

TELEPHONE CIRCLE 7-0100

July 16, 1947.

A. Brothman & Associates
85-03 57th Avenue
Elmhurst, Long Island.

Gentlemen:

Reference is made to phone conversation of several days ago regarding a high melting point having a low acid number which would be plastic at a temperature of 235°F.

Under separate cover we are forwarding to you a representative sample of Special Wax #1111 EX which has a U.T.D. melting point of 265°F and a softening point of 218°F. This wax should be plastic at about 220°F which would be the closest that we could come to the temperature you indicate.

Trusting that this wax will be satisfactory for the purpose that you have in mind and waiting the report of your test, we remain,

Very truly yours,

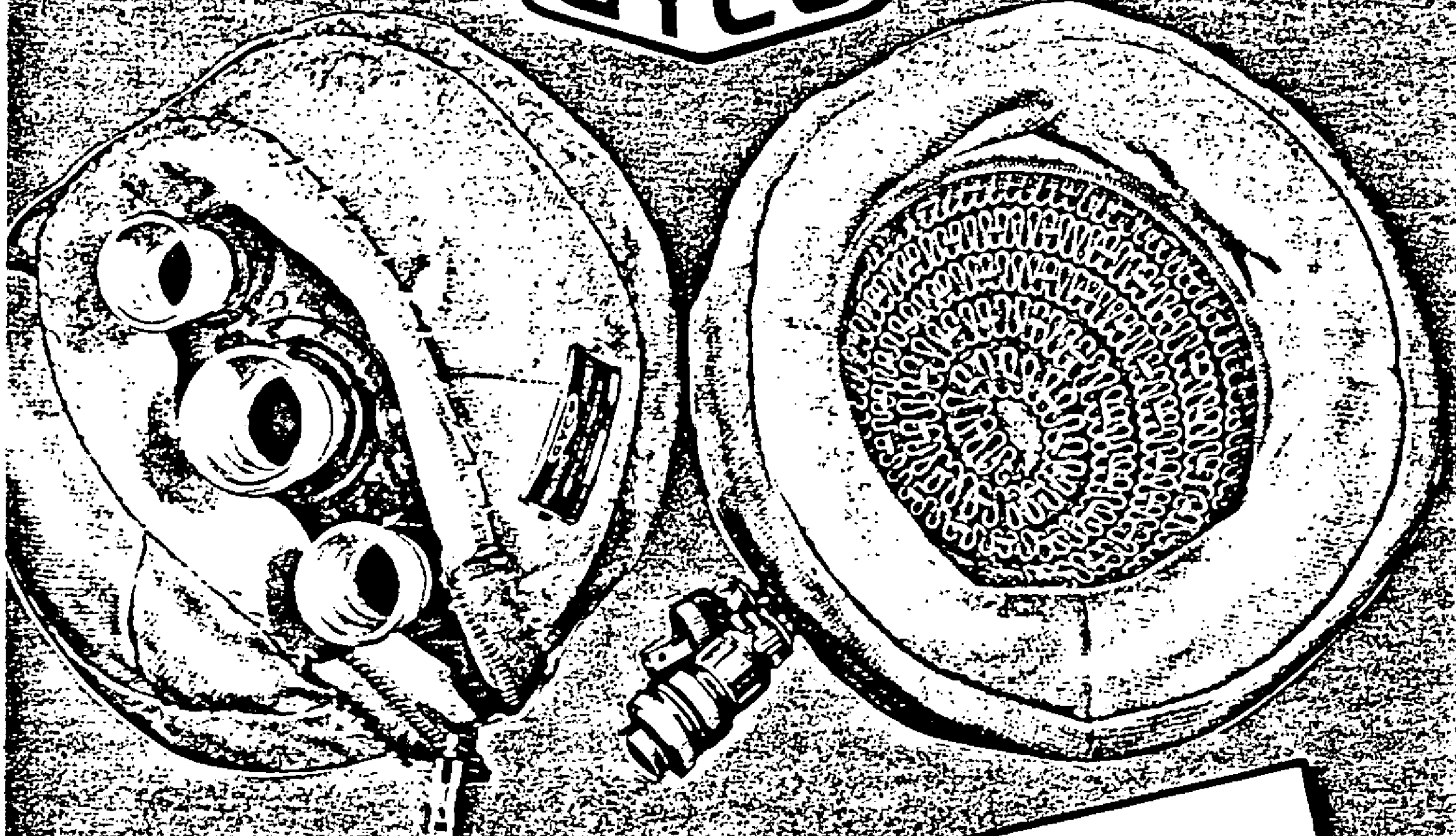
AMERICAN CYANAMID CO.

C. S. Bullock

C. S. Bullock

rf

GYCO

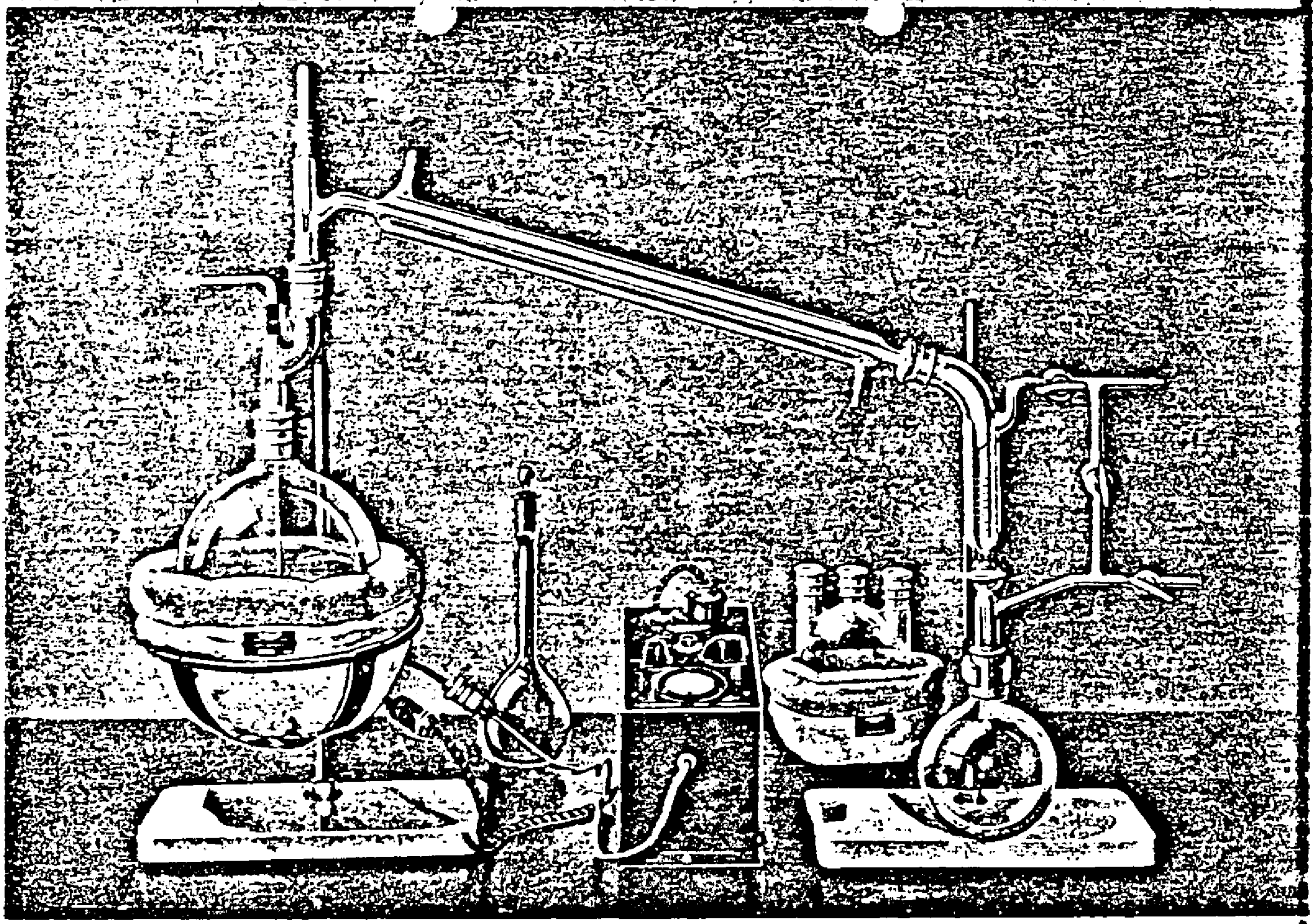


The Improved Heating Jacket

QUICK **ECONOMICAL** **SAFE**

GYCO Jackets are distributed exclusively by

CIENTIFIC GLASS APPARATUS CO., Inc.



GYCO Heating Jackets offer new advantages of safety and economy to meet the heating needs of every laboratory.

The heating jacket is constructed of highly insulating Fiberglas cloth and layers of Fiberglas wool, materials that are known for their durability under conditions of heat and moisture.

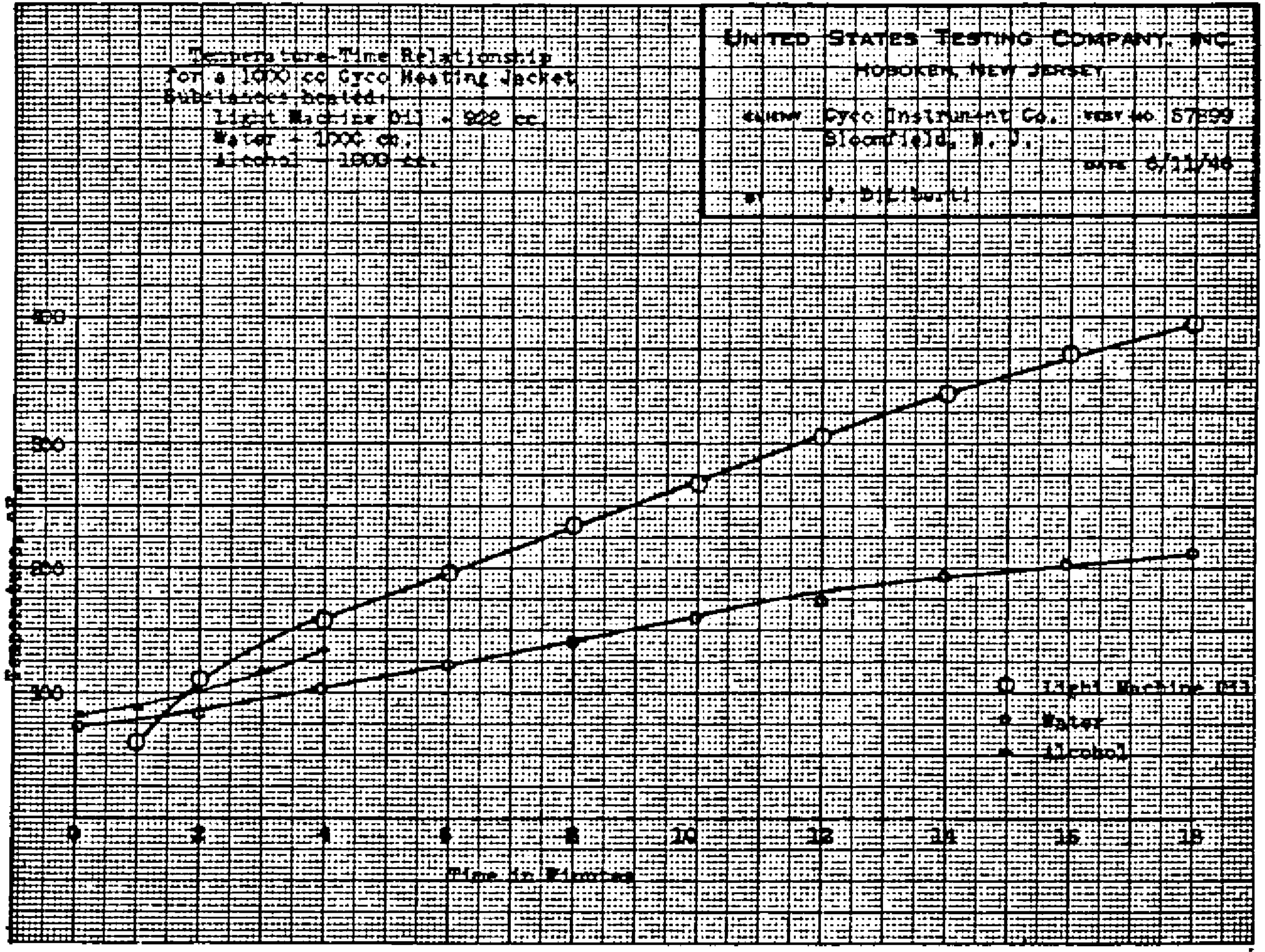
The construction and position of the heating elements provide the major innovation in the Gyco Heating Jacket. These elements, made of Safeway electrical resistance heating wire, are entirely insulated with glass yarn, then woven into a snake-like coil which is sewn with glass yarn in spiral fashion directly to the inner surface of the jacket. *The major economy achieved with this type of heating unit is the intimate contact of the elements with the vessel to be heated and the ease of constant control of temperature.* Using also more wire of the same wattage, surface temperatures are kept down, thus making the insulation more effective. The heating element can be operated below the visible glow point so that there is very little oxidation of the heating wire and no overheating of the insulation. Therefore, the life of the heating jacket is greatly increased. Heat control is achieved by using a Gyco Pyro-tran or any suitable variable transformer.

All Gyco Jackets have a built-in iron-constantan thermocouple, ending in an "AN" type iron-constantan plug for hooking up to the pyrometer of the Gyco Pyro-tran. (This plug may be removed for use with any other pyrometer of similar type.)

Gyco Heating Jackets will find many and frequent uses in most laboratories for fractionation, extraction, distillation or other processes requiring even constant heat.

Gyco Heating Jackets are made to fit all standard flask sizes, and special sizes can be made to order.

Since hemispherical units are most widely used, Gyco Jackets are standardized in that form. As an accessory we provide jacket tops which convert any Gyco Heating Jacket into a spherical unit. These jacket tops are available with elements for extra heat requirements or without elements for insulating purposes only. The tops rest securely



U.S. Testing Company Graph Showing Heating Speed of GYCO JACKETS

in place without need for troublesome lacings or slide fasteners around the jacket. A small vertical zipper opens the jacket top and permits removal of the top without disturbing the apparatus set up. All jacket tops with elements are furnished with a dual socket plug so that they may be connected with the jacket to the same transformer.

QUICK

The Gyco Heating Jacket was developed to fill the need for a faster and more efficient laboratory heating device. This jacket was submitted to an impartial organization for rigid tests. The graph reproduced above shows the speed of Gyco Heating Jackets in heating measured quantities of water, oil, and alcohol, as determined by the United States Testing Company, Inc., of Hoboken, N. J., in their report No. 57899 dated June 11, 1946. Your own comparison of these results with your present heating methods will prove that Gyco Jackets are superior.

SAFE

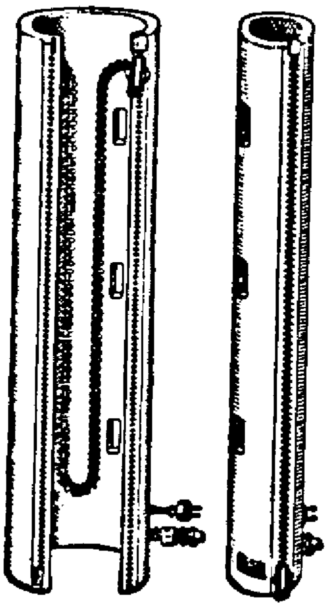
U. S. Testing Company, Inc., in safety tests to determine whether moisture from an overflowing or broken flask would damage the heater, found that the jacket operated even under water without apparent damage. In another test petroleum ether was poured over a jacket while in operation. Despite the inflammability of this material the non-glowing Safeway elements caused the ether to vaporize without bursting into flame. Light machine oil also was allowed to overflow onto the coils at high temperature without any ignition occurring.

For speed and safety, Gyco Heating Jackets will satisfy every need and be an excellent investment for any laboratory.

Gyco Jacket Tops make it unnecessary to dismantle apparatus when removing jacket. They convert a hemispherical jacket into a spherical and may be ordered separately.

GYCO TUBULAR

Heating Jackets



ntirely new in the heating mantle field is the Gyco ubular Heating Jacket. Construction and operation re for all practical purposes the same as for the Gyco lask Heating Jacket. Any laboratory columns which equire heat and insulation will be more efficient if covered ith a tubular jacket. Besides being less expensive than and-wound coils covered by asbestos and metal sleeves, ubular jacket heaters save weight as well as breakage. yco Jackets are especially valuable for fractional distillation where it is desirable to maintain the temperature f vapors rising in a column.

t the present, Gyco Tubular Heating Jackets are made n one- and two-foot lengths for 51- and 70-millimeter iameter jackets. For longer columns, two or more ibular jacket heaters can be combined to fit your reuirements. Slide fasteners make them easy to install r remove without disturbing your assembly.

PRICES ON GYCO TUBULAR JACKETS

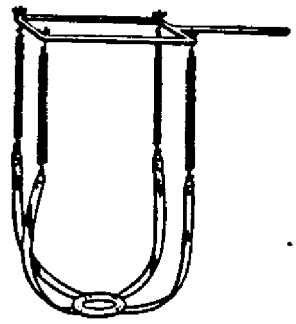
-300	For tube 70 mm. O.D. 12″ long........	$14.50
-310	" " 70 mm. O.D. 24″ long........	19.75
-320	" " 51 mm. O.D. 12″ long........	13.25
-330	" " 51 mm. O.D. 24″ long........	18.50

GYCO

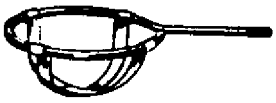
Jacket Supports

Specially designed supports are recommended for preserving the shape and insulation of Gyco Jackets.

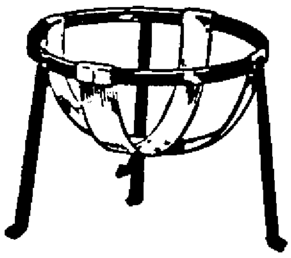
G-500	Cradle Support, will take jackets from 1 to 5 liter capacity.........	Each	$ 4.50
G-505	Tripod Support for 12-liter jacket.	Each	12.00
G-510	Tripod Support for 22-liter jacket.	Each	14.00
G-515	Tripod Support for 50-liter jacket.	Each	17.00
G-520	Tripod Support for 72-liter jacket.	Each	21.00



G-500



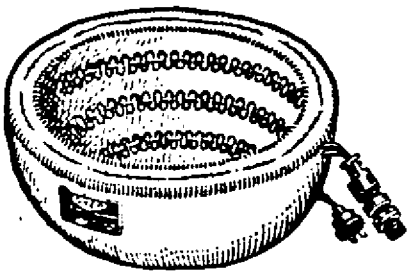
G-525



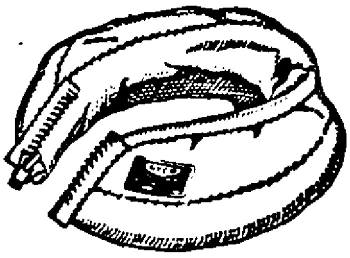
G-505-520

G-525	Extension Cradle Support for jackets 300 ml. and smaller...........	Each	$2.00
G-530	Extension Cradle Support for 500-ml. jacket......................	Each	2.75
G-535	Extension Cradle Support for 1-liter jacket..........................	Each	2.75
G-540	Extension Cradle Support for 2-liter jacket..........................	Each	2.75
G-545	Extension Cradle Support for 3-liter jacket..........................	Each	3.25
G-550	Extension Cradle Support for 5-liter jacket..........................	Each	3.75

GYCO HEATING JACKETS



HEMISPHERICAL JACKET



JACKET TOP

CATALOG NUMBER	FLASK SIZE	WATTAGE RATING	EACH
G-110	50	40	$ 6.65
G-120	100	110	7.45
G-130	200	245	9.75
G-140	250	245	9.75
G-150	300	245	10.65
G-160	500	300	11.65
G-170	1000	380	14.80
G-180	2000	550	16.70
G-190	3000	600	21.45
G-200	5000	675	26.25
G-210	12000	2-590	39.35
G-220	22000	2-700	47.05
G-230	50000	2-1250	76.25
G-240	72000	2-2000*	85.70

GYCO JACKET TOPS WITH ELEMENTS

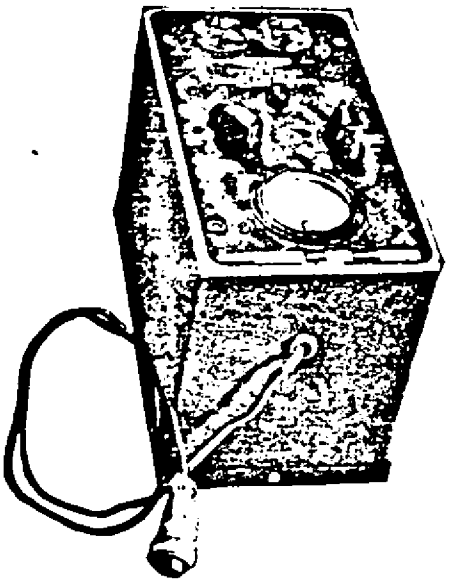
CATALOG NUMBER	FLASK SIZE	WATTAGE RATING	EACH
G-172	1000	90	$ 8.90
G-182	2000	138	9.80
G-192	3000	150	10.75
G-202	5000	300	13.10
G-212	12000	590	20.65
G-222	22000	650	29.95
G-232	50000	1000	42.75
G-242	72000	1000*	68.30

GYCO JACKET TOPS WITHOUT ELEMENTS

CATALOG NUMBER	FLASK SIZE	EACH
G-114	50	$ 4.15
G-124	100	4.80
G-134	200	5.50
G-144	250	5.90
G-154	300	6.20
G-164	500	6.60
G-174	1000	7.00
G-184	2000	7.45
G-194	3000	8.00
G-204	5000	10.30
G-214	12000	16.45
G-224	22000	23.00
G-234	50000	34.40
G-244	72000	57.15

* Available in 220 Volts only

GYCO Pyro-tran



FEATURES

- Positive Repeat Control
- Non-arcing
- Cool-operating
- Fuse-protected
- Built-in Pyrometer

TRANSFORMER and PYROMETER *in ONE Instrument*

The Gyco Pyro-tran is a new heavy-duty combination transformer and pyrometer. Although designed primarily to control temperatures in heating jackets, it can be used wherever a variable transformer is required. The Gyco Pyro-tran can operate at full power for a long period of time at high amperage load without any appreciable heat rise.

The principal feature of the Gyco Pyro-tran is the method of controlling voltages by two snap-type switches; one for primary adjustment and the other for vernier adjustment, giving approximately three volt step-ups. Thus, positive repeat voltage control is assured. This arrangement also eliminates coil type sliding contacts which arc and frequently burn out under load. Gyco Pyro-tran switches, made with ceramic housings, have silver plated contacts for long service, and are connected to the coil with strip copper take-off leads. Connections are made permanent by soldering.

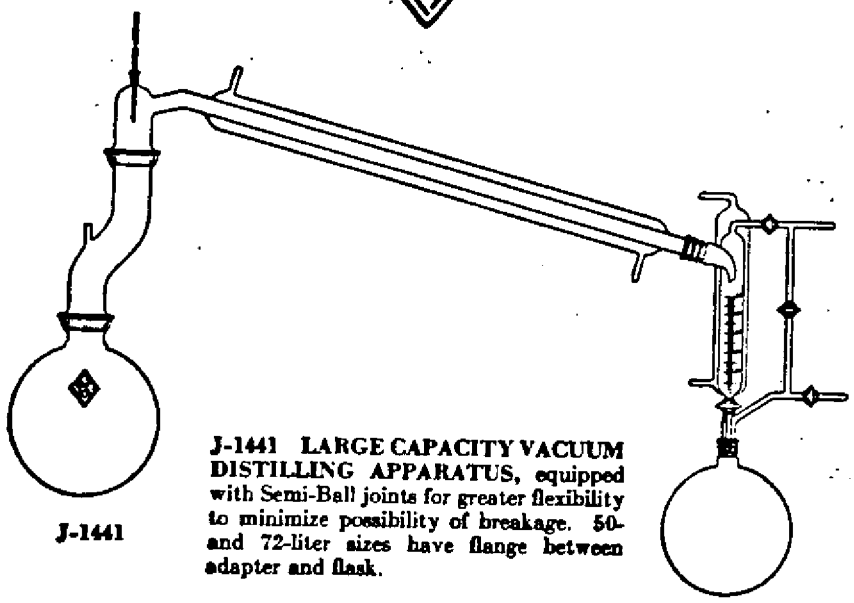
The Gyco Pyro-tran is provided with a heavy-duty rubber-covered input cable, and has twin plug outlet receptacles for connecting both a hemispherical jacket and cover or two hemispherical units at the same time and power. A red signal light shows when transformer is in operation. An easily replaceable fuse is provided to protect the instrument. Each Gyco Pyro-tran is fully insulated and is tested to five times the maximum working voltage to insure safe operation.

A Weston pyrometer is built into the Gyco Pyro-tran to indicate operating temperature up to 400° C. The dial has both Centigrade and Fahrenheit scales. A red line indicates the maximum operating temperature for heating jackets under all conditions. The pyrometer has an adjusting screw to compensate for room temperature. An iron-constantan fixed resistance wire lead, encased in a glass-impregnated sleeve, is installed to the pyrometer, with an "AN" type iron-constantan plug for hooking up to Gyco Heating Jackets. (This plug may be removed for use with any jacket not equipped with "AN" type plug.)

Gyco Pyro-trans are available in two models. Model H, for high range requirements, has a minimum of approximately 45 volts and a maximum of 122 volts, controlled in three-volt steps. Model L, for lower voltage requirements, has a range of 29 to 108 volts, in three-volt steps. Either model may be used for any combination of heaters or other equipment up to 2000 watts.

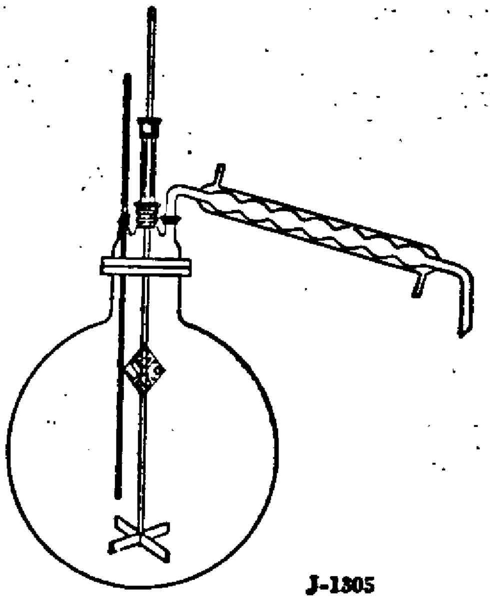
G-100	Gyco Pyro-tran, Model H........	$75.00
G-105	Gyco Pyro-tran, Model L........	75.00

NEW GLASS SPECIALTIES



J-1441

J-1441 LARGE CAPACITY VACUUM DISTILLING APPARATUS, equipped with Semi-Ball joints for greater flexibility to minimize possibility of breakage. 50- and 72-liter sizes have flange between adapter and flask.



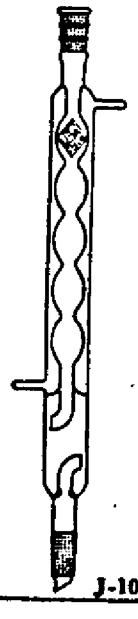
J-1305

J-1441 LARGE CAPACITY VACUUM DISTILLING APPARATUS*

Flask size in ml.	Condenser length	Ŧ	Price Complete	Condenser only	Adapter only	Receiver only	Receiving flask only	Thermometer only	Clamps only
22000	30″	34/45 & 102/75	$ 91.25	$24.00	$15.00	$19.00 (100 ml.)	$ 6.90 (12 l.)	$3.85	$ 5.00 (2)
50000	30″	"	107.35	24.00	14.00	22.00 (250 ml.)	14.00 (22 l.)	3.85	10.00 (2)
72000	36″	"	121.85	28.00	14.00	22.00 (250 ml.)	14.00 (22 l.)	3.85	10.00 (2)

J-1305 LARGE CAPACITY DISTILLING APPARATUS*

Flask size in ml.	Condenser length	Price complete	Adapter only	Condenser only	Stuffing box only	Stirrer only	Thermometer only	Clamp only	Flask only
22000	30″	$86.77	$15.00	$15.00	$17.77	$6.50	$ 7.50	$7.50	$17.50
50000	30″	89.75	15.00	15.00	17.77	7.00	8.50	7.50	19.00
72000	36″	107.27	15.00	20.00	17.77	7.50	10.00	7.50	29.50



J-1039

J-1039 NO-FLUD Reflux Condenser (patented). A new type of reflux condenser with built-in trap to prevent "slugging" or "flooding."

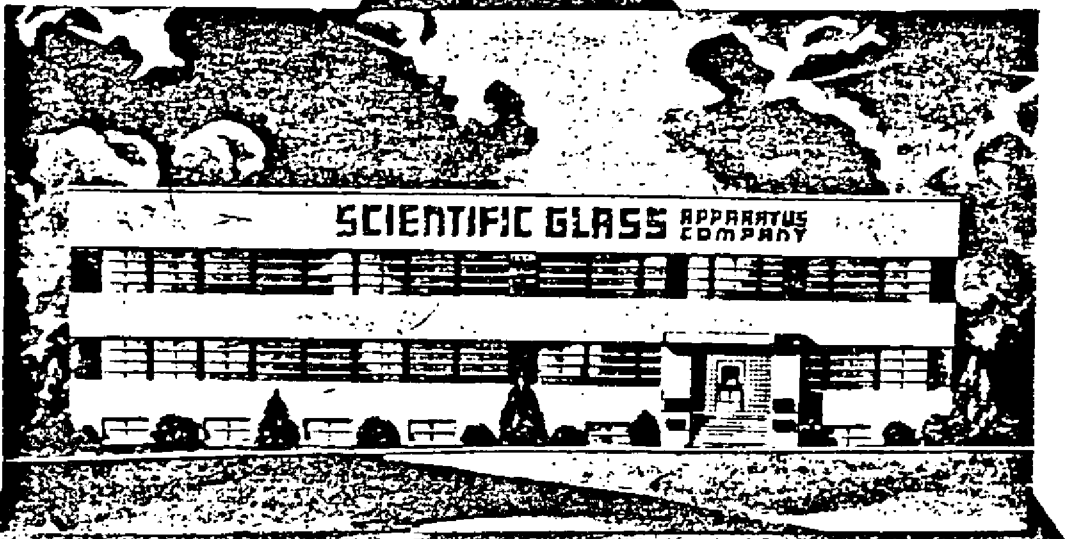
Condenser length	Ŧ 19/38	Ŧ 24/40	Ŧ 29/42
25 cm.	$10.50	$10.75	$11.25
30 cm.	11.00	11.25	11.75
40 cm.	11.50	11.75	12.25
50 cm.	12.25	12.50	13.00
60 cm.	12.75	13.00	13.50
90 cm.	15.75	16.00	16.50

J-1058 NO-FLUD Column (patented) with silvered jacket and honeycomb packing support. Construction eliminates "flooding" or "slugging."

Column length	Ŧ 24/40	Ŧ 29/42
30 cm.	$16.50	$17.00
45 cm.	18.00	18.50
60 cm.	20.00	20.50
90 cm.	22.50	23.00
120 cm.	27.00	27.50

J-1058

* Sold subject to U. S. Internal Revenue Regulations.

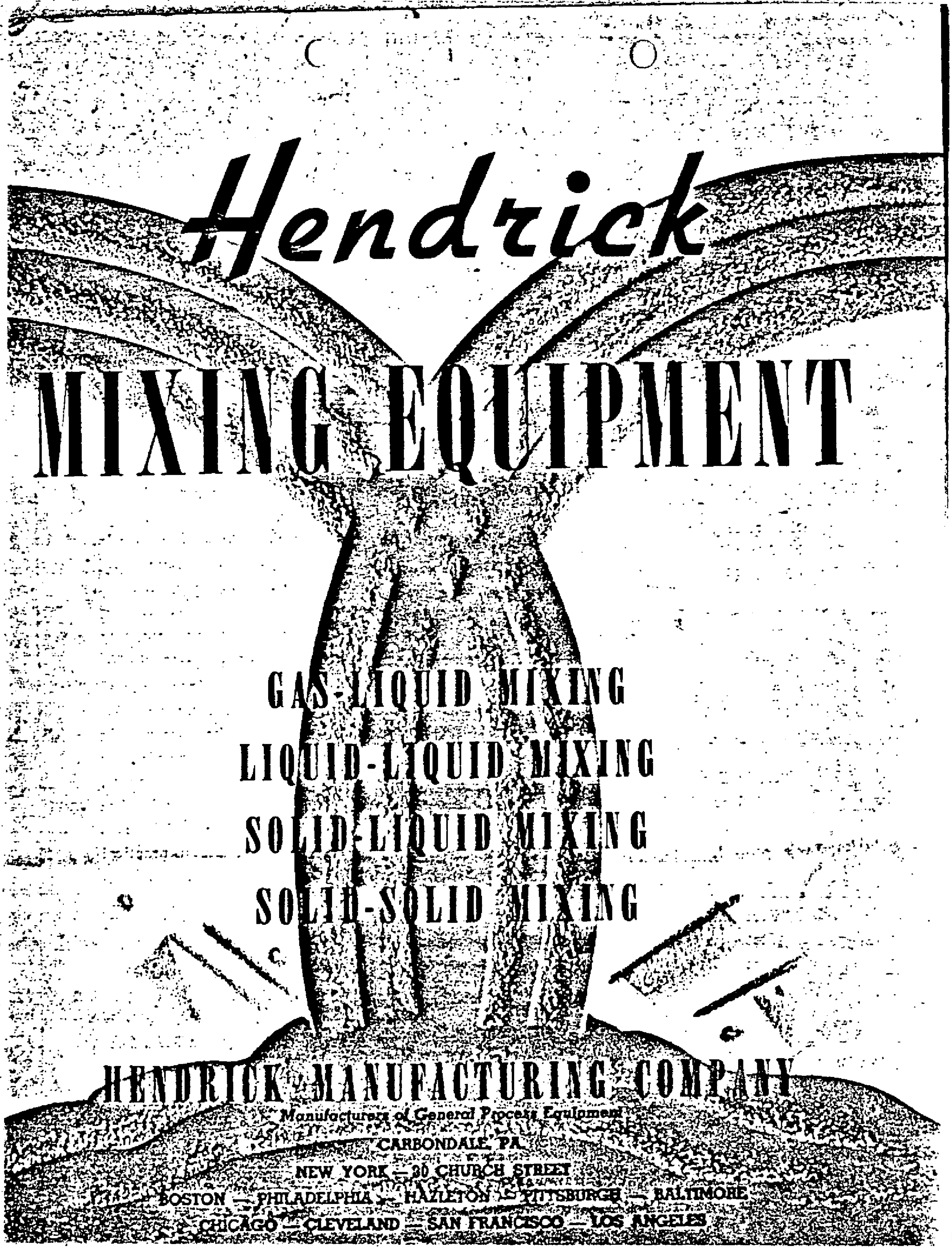


In addition to a large and varied stock of laboratory apparatus and supplies, we have complete facilities for the manufacture of all types of special glass apparatus.

SCIENTIFIC GLASS APPARATUS COMPANY, INC.

BLOOMFIELD NEW JERSEY

C-100-946
Printed in the U. S. A.



Hendrick

MIXING EQUIPMENT

GAS-LIQUID MIXING
LIQUID-LIQUID MIXING
SOLID-LIQUID MIXING
SOLID-SOLID MIXING

HENDRICK MANUFACTURING COMPANY
Manufacturers of General Process Equipment
CARBONDALE, PA.
NEW YORK — 30 CHURCH STREET
BOSTON — PHILADELPHIA — HAZLETON — PITTSBURGH — BALTIMORE
CHICAGO — CLEVELAND — SAN FRANCISCO — LOS ANGELES

FOREWORD

Authorities* agree that the art of mixing, in all its various aspects, for years failed to keep step with the development of other elementary chemical engineering practices. In recent years, however, efforts have been made to raise the major phases of mixing, mixing selection and mixer mechanical design, to a position more in keeping with the widespread use and importance of mixing. Some idea of the scope of work done by Hendrick engineers in the advancement of the art may be gained from the following bibliography of contributions by members of the Hendrick engineering staff:

- "Choice of Emulsifiers"—May, 1939, Chemical and Metallurgical Engineering
- "Introduction to Liquid Mixing"—October, 1939, Chemical and Metallurgical Engineering
- "Resin Plant Design"—October, 1939, Modern Plastics
- "Mixing Operations in the Paint and Pigment Industries"—October, 1939, National Paint Bulletin
- "Vertical Shaft Design for Balanced Rotors with Calculations for High Speed Rotor Effects — April, 1940, Product Engineering
- "Stuffing Box Design—September and November, 1940, Product Engineering

Efficient mixing is dependent upon the selection of the proper type of mixing unit as well as the correct mechanical design of the chosen mixer assembly. These twin aspects cannot be separated. Again, as a guide in the selection and design of mixing equipment, cited above, attention is directed to the bibliography.

The types of mixing equipment described in this catalog are, as far as possible, presented under the headings of the various elementary binary mixing systems; gas-liquid, liquid-liquid, solid-liquid, solid-solid mixing. Wherever possible, specific operations to which a particular mixer is suited are listed. These lists, however, are not intended to be complete. They are merely guides for the selection of the type of mixer best suited to individual requirements. Within the limitations of space, an effort has been made to present the material in such form that it will constitute a practical manual on mixing operations.

Hendrick engineers will gladly cooperate with you in the selection and design of mixing equipment best suited to your requirements. They will, upon request, submit detailed recommendations.

HENDRICK MANUFACTURING COMPANY

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*Chapter 16, Chemical Engineers Handbook, 1934 Edition.

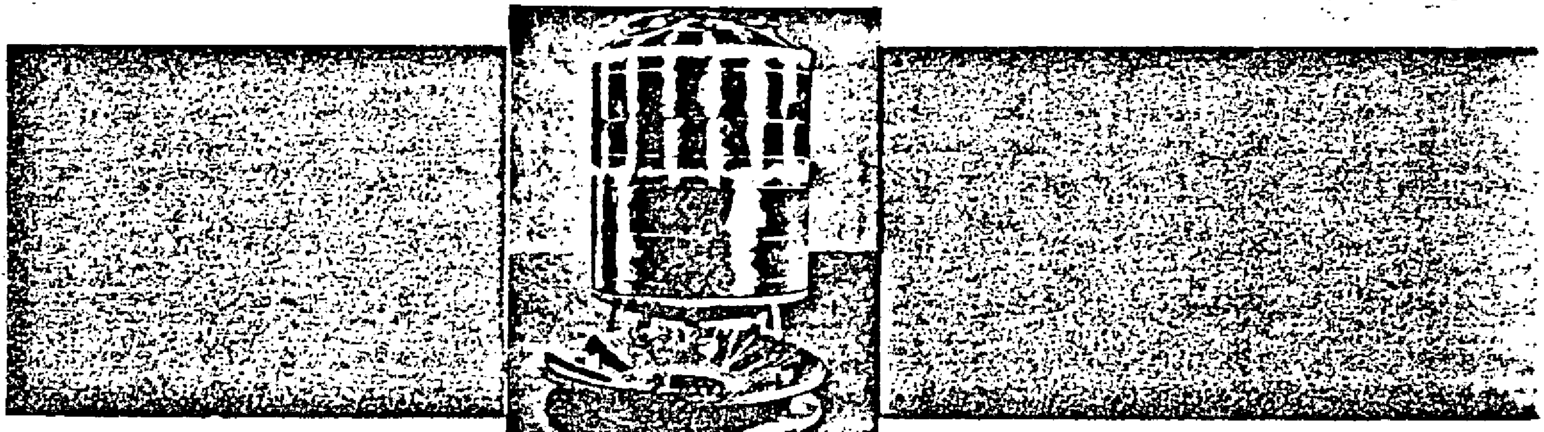
Printed in U.S.A.

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.

SOME EXAMPLES OF TIME-SAVING, COST-REDUCING PERFORMANCES OF HENDRICK MIXING EQUIPMENT

In a well-known chemical plant a Hendrick Injection Mixer, chlorinating large batches of an aromatic hydrocarbon, has cut the operating time from 22 hours to 7½ hours.

In four pilot plant demonstrations, for four different companies, Hendrick Injection Mixers, accomplished the air-bodying of various grades of linseed oil at varying temperatures in 1/3d to 1/6th the time previously required:

- —an 18 hour cycle at 250°F. was reduced to 7¼ hours
- —a 60-70 hour cycle at 95°F. was decreased to 22 hours
- —a 24 hour cycle at 212°F. was cut to 4 hours
- —bodying of linseed oil at 175°F. to 195°F. was reduced to 1/3d the time previously required.

In another well-known company, Hendrick Injection Mixers effected the absorption of carbon dioxide by a washing solution in 1/5th the time previously required.

In the sulphonation of cocoanut oils, Hendrick Injection Mixers are producing a more uniform product with a 30% reduction in the time cycle.

In the caustic refining of vegetable oils, a Hendrick Injection Unit in a Hendrick Continuous Mixer assembly delivered a throughput of 12 gallons per minute, exceeding the throughput of another type of equipment occupying three times the floor space.

In the dissolving of soda ash in a black liquor process, a Hendrick Continuous Dissolving assembly incorporating a Hendrick Super-Turbine Mixing Unit, has materially reduced the cost of maintaining a high throughput.

A Hendrick Super-Turbine Mixer in a resin thinning tank has effected a 50% reduction in the time required to dissolve the resin, with a corresponding saving in the cost of operation.

A Carnauba-water emulsion, requiring an average of 7 hours to prepare with a paddle mixer, was produced to an equivalent state of dispersion and lasting properties in 10 to 12 minutes in a mixer assembly employing a Hendrick Super-Turbine Mixing Unit.

The Importance of Kettle Design

Efficient mixing is dependent upon two inter-related basic factors: selection of the type of mixer best adapted to the requirements of the particular problem; the suitability of the containing kettle to the most efficient operation of the agitator unit. The inter-relationship of these factors demands that the design characteristics of a mixer (the speed and location of members) be determined with respect to the shape and dimensions of the containing kettle, and also that the design of the kettle be consistent with the optimum design characteristics of the mixer.

Inadequate complementing of these two basic factors may result in packing of solids or viscous masses in kettle corners or similar areas of "secondary turbulence", material reduction from the best possible rate of heat transfer, and marked increase in the time required to complete the mixing operation.

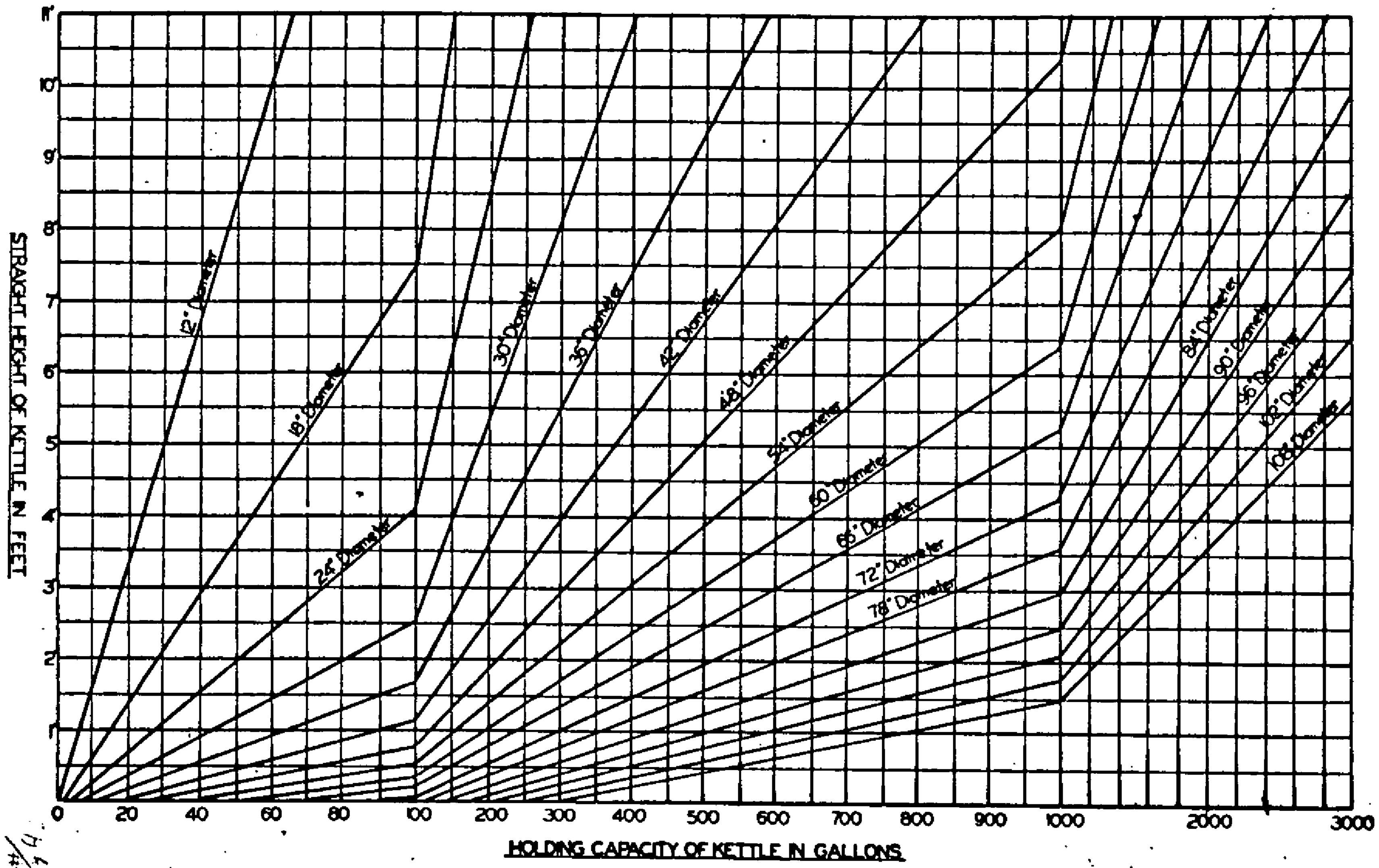
The importance of the best possible coordination of kettle design and mixer design is most definitely demonstrated in instances where processes developed in laboratory or pilot equipment are carried over to commercial production. In such cases, the critical aspects of the processing sequence, cooling or heating cycles and the rate of "contacting" of reactants established, are frequently dependent upon the consistent reproduction of mixing conditions.

The design of a kettle is frequently determined by floor space and ceiling height, weight and plate thickness requirement considerations, required areas of contact in heat transfer problems, and other processing or external conditions. Similarly, the design characteristics of the Mixer unit may be arbitrarily determined by cleaning and other considerations, by the optimum speed range of the mixer, etc.

Regardless of whether your problem calls for a replacement mixer for an existing vessel or for a complete Autoclave, Resin Kettle or other assembly, Hendrick engineers will gladly consult with you on the coordination of all factors of design.

When new equipment is being installed, the coordinated assembly of a Hendrick Mixer in a Hendrick Processing Vessel will assure maximum efficiency and economy.

Hendrick Processing Vessels are welded in accordance with the governing provisions of the ASME and API-ASME codes for pressure vessels. Our fabrication facilities make possible the construction of any size of vessel starting from a fraction of a gallon and extending through the largest commercial sizes.


STRAIGHT HEIGHT OF KETTLE IN FEET
HOLDING CAPACITY OF KETTLE IN GALLONS
11'
10'
9'
8'
7'
6'
5'
4'
3'
2'
1'
0
20
40
60
80
100
200
300
400
500
600
700
800
900
1000
2000
3000
12" Diameter
18" Diameter
24" Diameter
30" Diameter
36" Diameter
42" Diameter
48" Diameter
54" Diameter
60" Diameter
66" Diameter
72" Diameter
78" Diameter
84" Diameter
90" Diameter
96" Diameter
102" Diameter
108" Diameter

Hendrick Injection Mixer

Gas-Liquid Mixing:

Gas-liquid mixing operations may be classified broadly into (a) rapid or instantaneous absorption or reaction of the distributed gases; (b) medium absorption or reactivity; (c) difficult or slow absorption or reactivity. Gas-liquid mixing problems should also be considered from the standpoints of quantity and rate of gas distribution required, and the pressure and temperature in the system under which the distribution is effected.

Three principal factors generally determine the velocity of a gas-liquid reaction:

1. The physical properties of the liquid as they affect the ability of the liquid to retain the distributed gas.
2. Solubility of the gas in the liquids under the prevailing processing conditions of temperature and pressure.
3. The area of interphase contact between gas and liquid phases.

Hendrick Injection Mixer was specifically developed for gas-liquid mixing, especially the more complicated and critical types. The ability of the injection mixer to effect increased reaction velocities, economies of reagent, and positive control over the progress of the gas-liquid mixing operation is due to:

- —Uniform processing and rapid circulation of the entire contents of the mixing tank.
- —Direct mechanical shearing of the gas-injected liquid.
- —High secondary shearing of the distributed bubbles through the setting up of high liquid velocities.

Structurally, the Hendrick Injection Mixer (Fig. 1) consists of a specially designed turbine agitator rotor which is overhung and underhung by hollow ring-shaped stators. The turbine exerts a pumping action on the contents of the mixing vessel (Fig. 2), drawing in through top and bottom impeller inlets and delivering centrifugally over the entire periphery of the turbine. The gas or other treating agent is fed to the hollow stators through the indicated pipe feeds and is discharged through perforations on the rotor-faced surfaces of the stators.

As the liquid passes between the stators and the rotor it exerts a spatula action on the gas discharged through the bubble holes. The gas-injected liquid is then subjected to a shearing action between the radial ribs on the stators and the turbine blades. The combination of the spat-

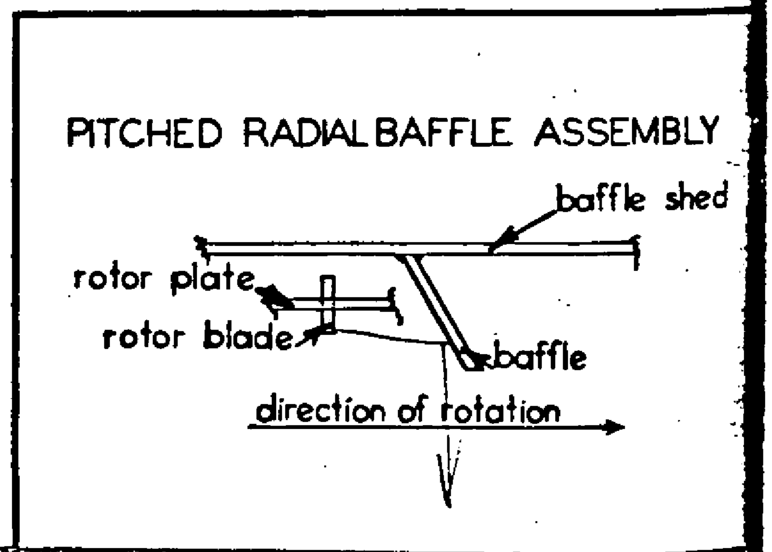


Fig. 3. Side elevation, Hendrick "pitched" radial Baffle Assembly.

ula action and the shearing of the bubbles results in a complete and instantaneous dispersion of the gas. The high pumping capacity of the rotor insures a rapid re-circulation of the tank contents and hence a continuous re-processing of the liquid.

Additional design refinements of the basic structure of the Hendrick Injection Mixer include the Hendrick "pitched" radial baffle assemblies (Fig. 3), circumferential delivery muffling cages (Fig. 1), draft-tubes, etc. The "pitched" radial baffle assembly consists of a number of radially disposed baffle plates so arranged with respect to the turbine rotor that they offer a downward directing influence on the gas-injected liquid. When the gas-retention properties of the liquid are low, the uniformity of contact of gas and liquid and the time of contact are increased through the lengthening of the linear path traveled by the dispersed bubbles.

Hendrick Injection Mixers may be surrounded by circumferential delivery muffling cages for the purpose of enhancing the direct mechanical shearing through the impeding of the turbine pumping action.

Hendrick draft-tube assemblies differ in design, according to the specific requirements of each problem. In general, these draft-tube units perform three basic functions:

Prevent short-circuiting of the agitated liquid by developing a positive vertical motion in the liquid mass.

Cause a forced draft through the coil banks, when internal coils are involved, thus increasing the rate of heat transfer.

Define the path of the freshly added liquid phase in continuous mixing operations in kettles equipped with overflow weirs.

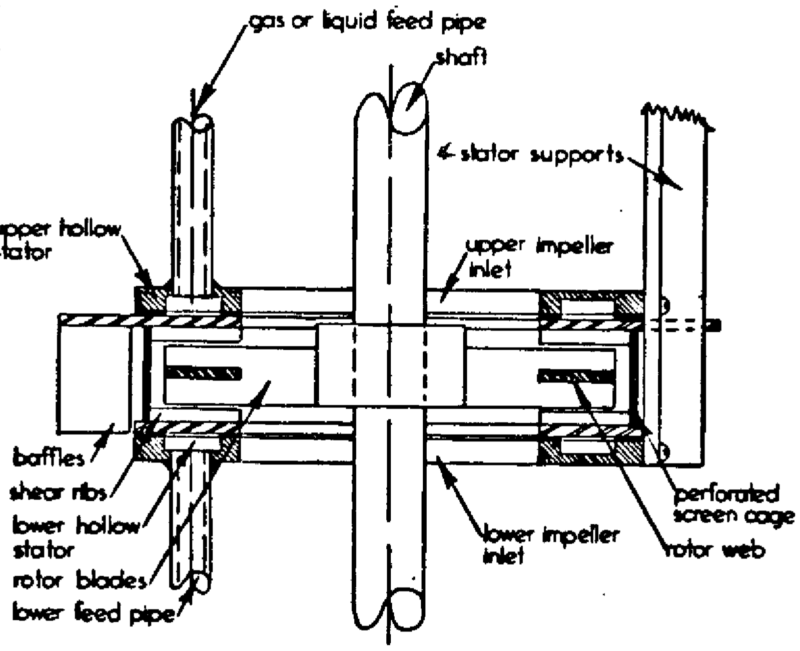


Fig. 1. Hendrick Injection Mixer.

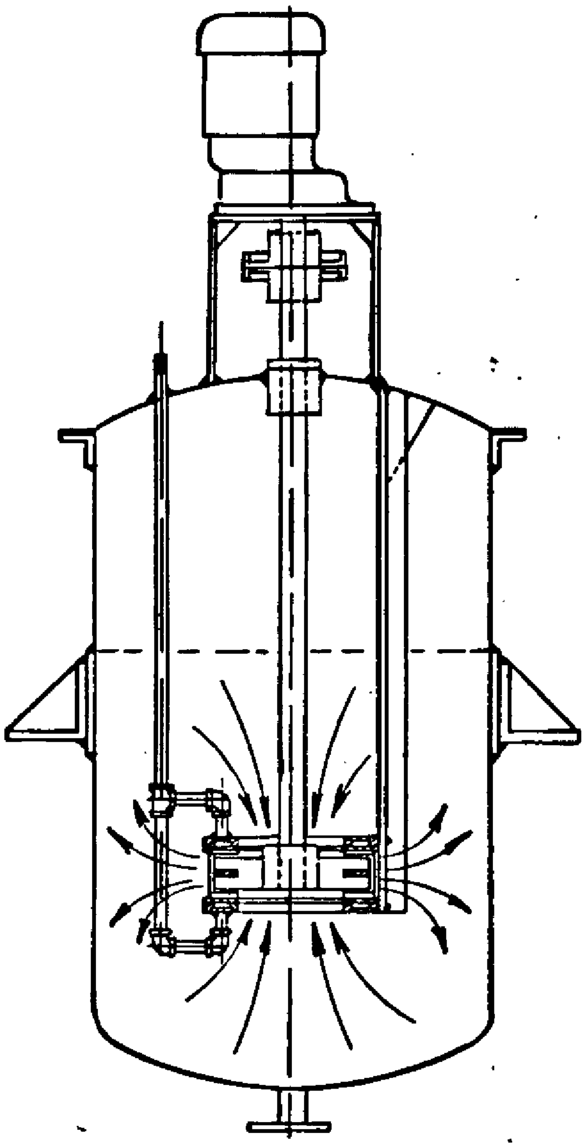


Fig. 2. Hendrick Injection Unit in reaction vessel.

Arrows indicate main flow directions set up by Mixer unit. See Text.

HENDRICK INJECTION MIXERS OFFER INCREASED EFFICIENCY AND REDUCED COST OF OPERATION IN THE FOLLOWING TYPICAL APPLICATIONS:

- Hydrogenations of oils and other liquids
- Oxidations of oils and dyestuffs
- Aerations of liquids
- Sulphonations involving SO_3 as the sulphonating agent
- Halogenations of liquids
- Blowing of oils
- Gas-scrubbing and flue-gas absorption
- Gas-gas reactions taking place in a common liquid bath
- Gas bleaching of juices, oils, etc.
- Mineral ore flotation
- Blowing of asphaltum
- Steam distillation of volatiles as in the deodorization of vegetable oils
- Washing sulphur out of natural gas
- Sulfite liquor preparation
- Carbon dioxide absorption

Liquid-Liquid Mixing:

The Hendrick Injection Mixer, by reason of its basic design and method of operation, is ideally suited to sulphonations, nitrations, and other mixing operations characterized by the following requirements:

Instantaneous dispersion of the added reagent

Absolute freedom from over-concentration of reagent

Positive control over the rate of progress of the operation

The fact that the Injection Mixer accomplishes the introduction and primary dispersion of the added liquid at the point of most intense mixing action:

—prevents local over-concentration of the added liquid

—nullifies the influence of large differences in consistency and specific gravity between the treated and treating phases

—Overcomes the absence of diffusion currents as an auxiliary aid to rapid and instantaneous dispersion in instances of immiscible liquids

Since the velocities of many chemical reactions are determined by the rapidity with which the reacting materials are brought into contact with one another, the high pumping capacity of the Hendrick Injection Mixer and its complementary direct mechanical shearing action tend to reduce the time and cost of the operation.

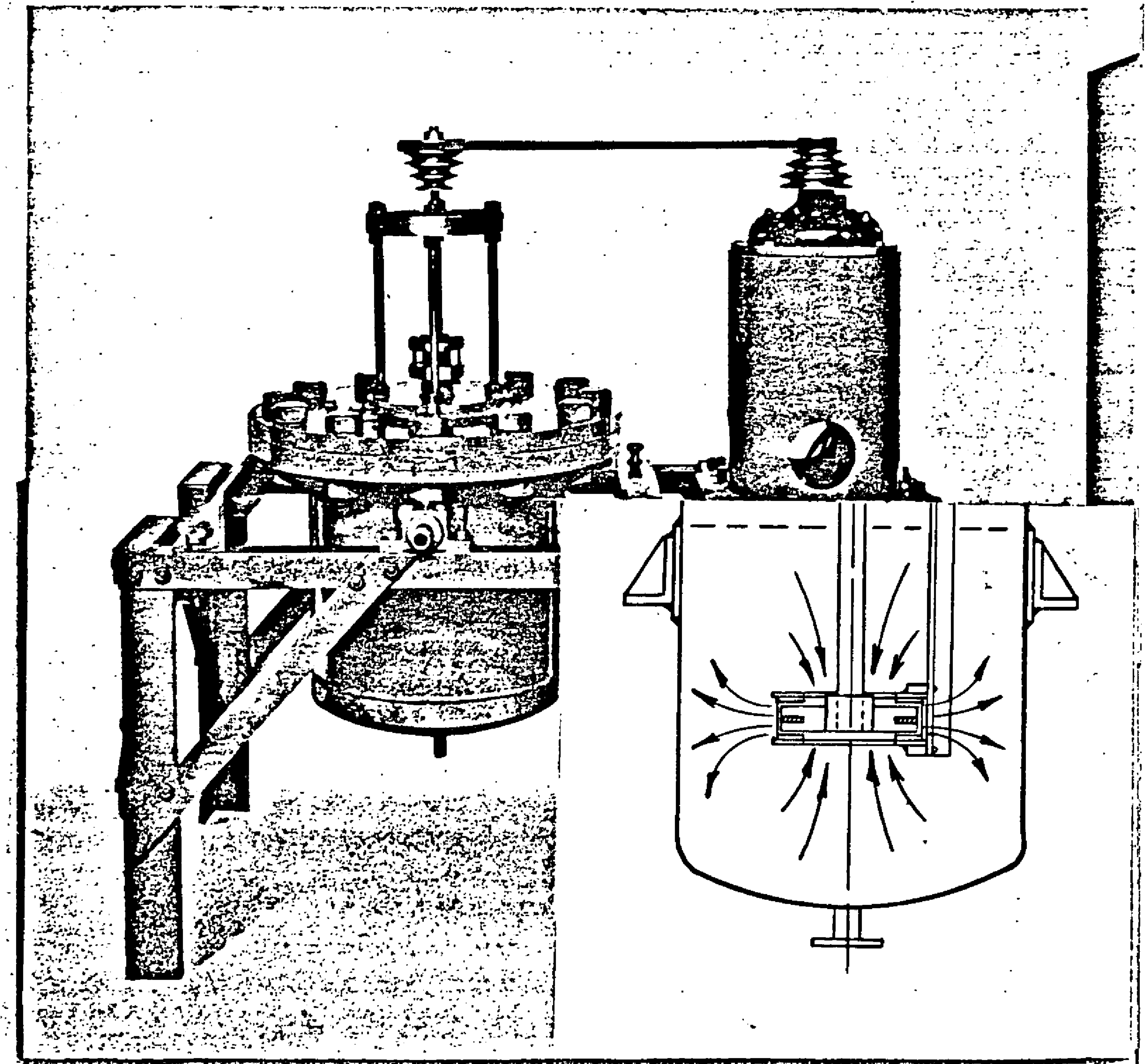
The Hendrick Injection Mixers are being used with material economies in the cost of the operation and substantial reductions in mixing time for:

- Sulphonations of oils and other organics
- Nitration of organics
- Acid treating of lubricating oils
- Caustic refining of vegetable oils
- Sulphuric acid contacting of gasolines in the polymerization of butene in the production of high octane aviation gasoline

Hendrick Injection Mixers are furnished in all commercial metals, and also in rubber-clad, as replacement units for existing vessels or as integral parts of Hendrick Autoclaves, Resin Kettles, Hydrogenators, Chlorination Assemblies, etc.

Hendrick Injection Type Mixers are available in the following standard sizes:

2", 4", 6", 9", 12", 18", 24", 30", 36", 42", 48", 54" and 60" rotor diameter units.



300 pounds per square inch W.P. Autoclave employing Hendrick Injection Mixer, built for hydrogenation of edible oils.

Hendrick Super-Turbine Mixer

The Hendrick Super-Turbine Mixer was developed specifically to handle with increased efficiency such liquid-liquid and solid-liquid mixing problems as:

—Dissolving of cotton, gums, and that class of materials which take on a jelly-like character on contact with solvents.

—Preparation of suspensions, emulsions, supersaturated solutions, slurries, pulps, etc.

—Blending and thinning of lacquers, paints, enamels, etc.

—Thinning and blending of resins.

—Agitation of heterogeneous reaction systems.

—Blending of components varying greatly in viscosity, specific gravity, set.

—Distribution of gums and resins in paints, lacquers, enamels.

—Clay and activated carbon contacting of lubricating and vegetable oils.

—Incorporation of pigments in water or other vehicles in the preparation of pigment dispersions.

—Premixing in paint manufacturing operations.

The Hendrick Super-Turbine Mixer (Fig. 4), consists of a specially constructed turbine agitator rotor which is overhung and underhung by stator ring-plates. The stators have impeller inlets through which the tank liquid, and particles suspended therein, are drawn into the mixer unit (Fig. 5). The turbine functions to develop the aforementioned suction action and to circulate the mixing vessel contents. As in the case of the Hendrick Injection Mixer, the Super-Turbine stators have on their

its basic design and method of operation, is ideally suited to sulphonations, nitrations, and other mixing operations characterized by the following requirements:

Instantaneous dispersion of the added reagent

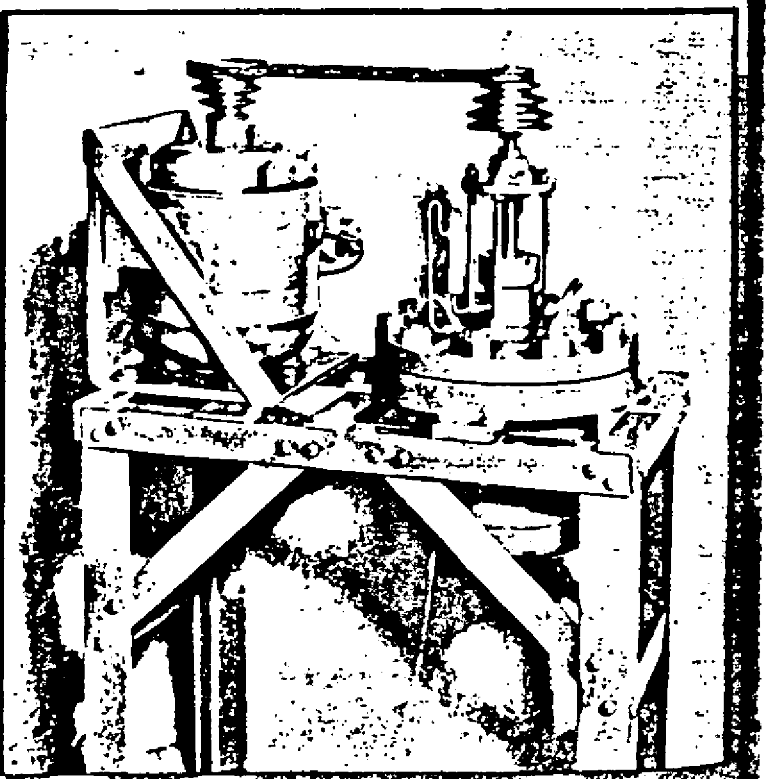
Absolute freedom from over-concentration of reagent

Positive control over the rate of progress of the operation

The fact that the Injection Mixer accomplishes the introduction and primary dispersion of the added liquid at the point of most intense mixing action:

—prevents local over-concentration of the added liquid

Fig. 4. Hendrick Super-Turbine Mixer



500 pound per square inch laboratory autoclave equipped with Hendrick Injection Mixer and using the Hendrick hydraulically sealed external and internal stuffing boxes.

tor-faced surfaces a number of radially disposed s which act as shearing complements to the turne blades. The tank liquid in circulating through e mixer is subjected to a shearing action between e stator ribs and rotor blades.

The coupling of the high fluid velocities proced by the turbine, together with its direct meanical action offered by the mixer as a whole, relts in sharp reductions in the cost of and time quired for many mixing operations.

Hendrick Super-Turbine Mixers are furnished in her Uni-Turbine or Multi-Turbine arrangents (Fig. 6), according to the individual requirents of each size and shape of tank.

The basic structure of the Super-Turbine Mixer sometimes modified to suit the specific requirents of certain mixing systems. Typical of such odifications are the use of delivery-muffling ges, radial baffle assemblies and draft-tubes.

The Hendrick Super-Turbine Mixer is furnished all commercial metals, and also in rubber-clad, incorporation in existing mixing vessels or as egral portions of Hendrick Thinning, Dissolv-, Blending, or Emulsification Units. The Mixer available in the following standard rotor diameter its:

", 4", 6", 9", 12", 18", 24", 30", 36", 42", 48", 54", 60".

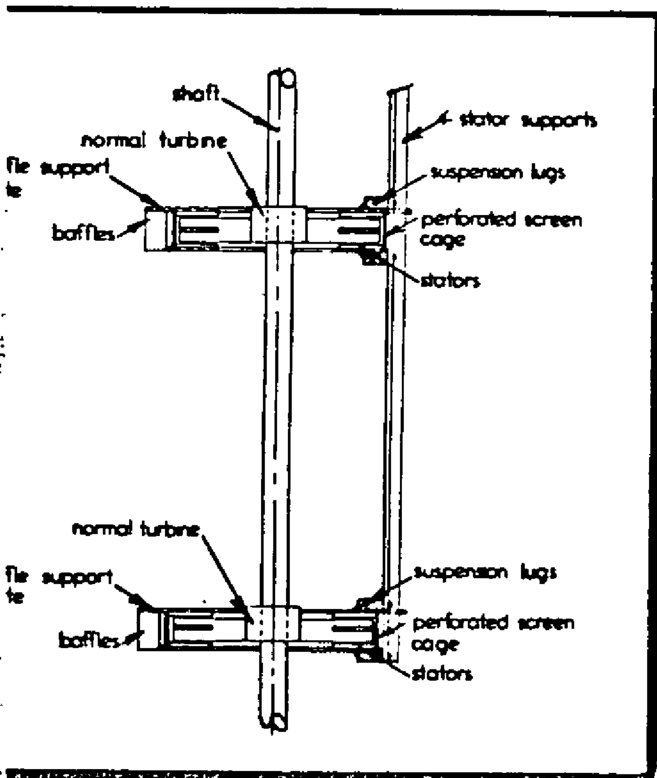


Fig. 6. Hendrick Super-Turbine units in multi-turbine arrangement.

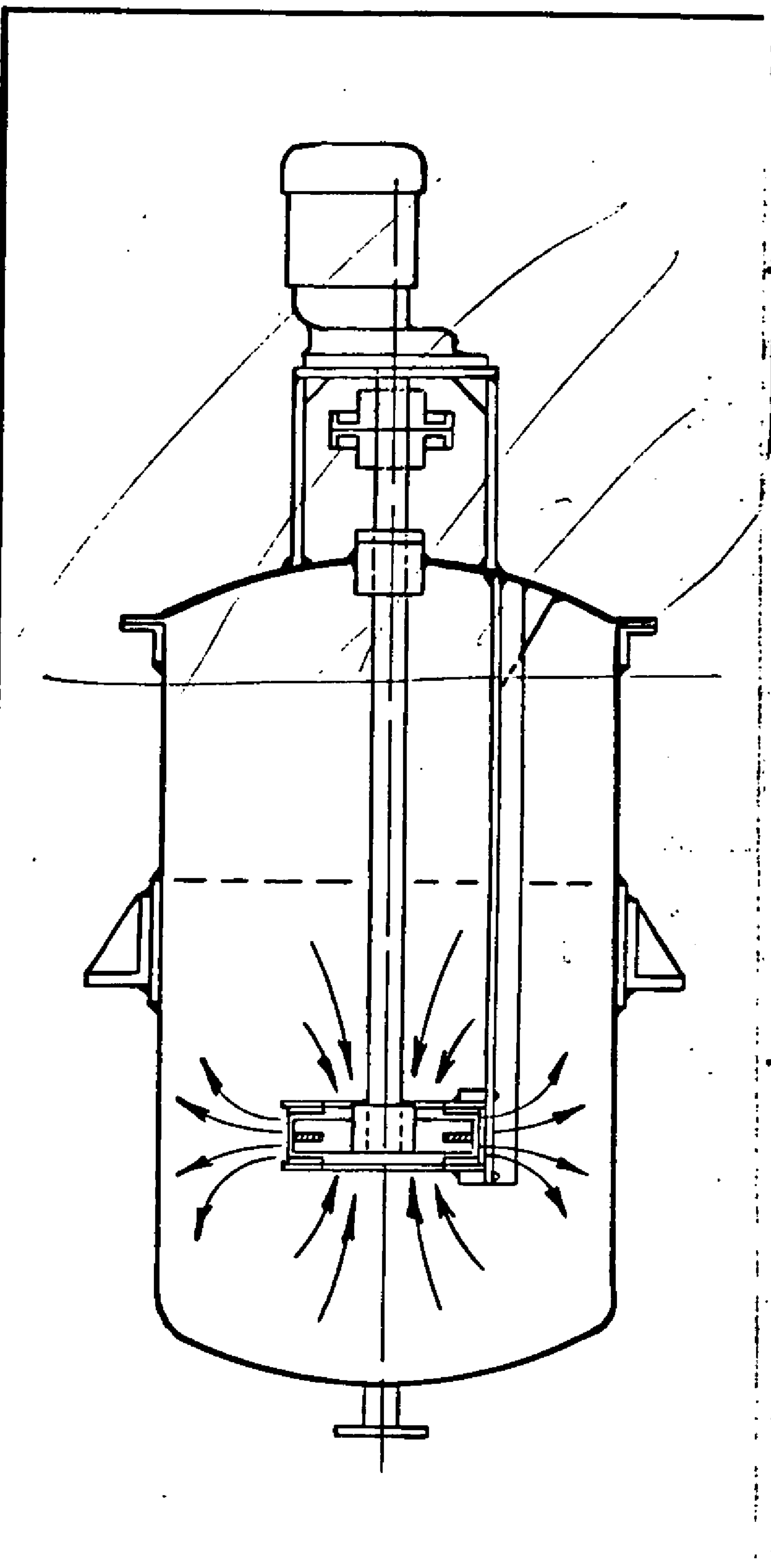


Fig. 5. Hendrick Uni-Super-Turbine Mixer in thinning tank. Arrows indicate main flow directions set up by Mixer unit. See Text.

Hendrick Normal Turbine Mixer

The Hendrick Normal Turbine Agitator (Fig. 7) is an all-welded construction turbine wheel consisting of a number of blades welded to a hub, the individual blades being braced against tangential displacement by a re-inforcing ring located near the hub.

The Hendrick Normal Turbine is well adapted to those special mixing problems in which a high rate of translation of the tank contents is the exclusive basic requirement, and in which the direct mechanical shearing action afforded by either the Super-Turbine or Injection Type Mixers is of negligible importance. The Normal Turbine Mixer is thus well suited to:

- Dissolving problems in which readily soluble materials added in a fine state of division are involved.
- The agitation of slurries or suspensions in which no reduction in the particle-size of the solid component is demanded.

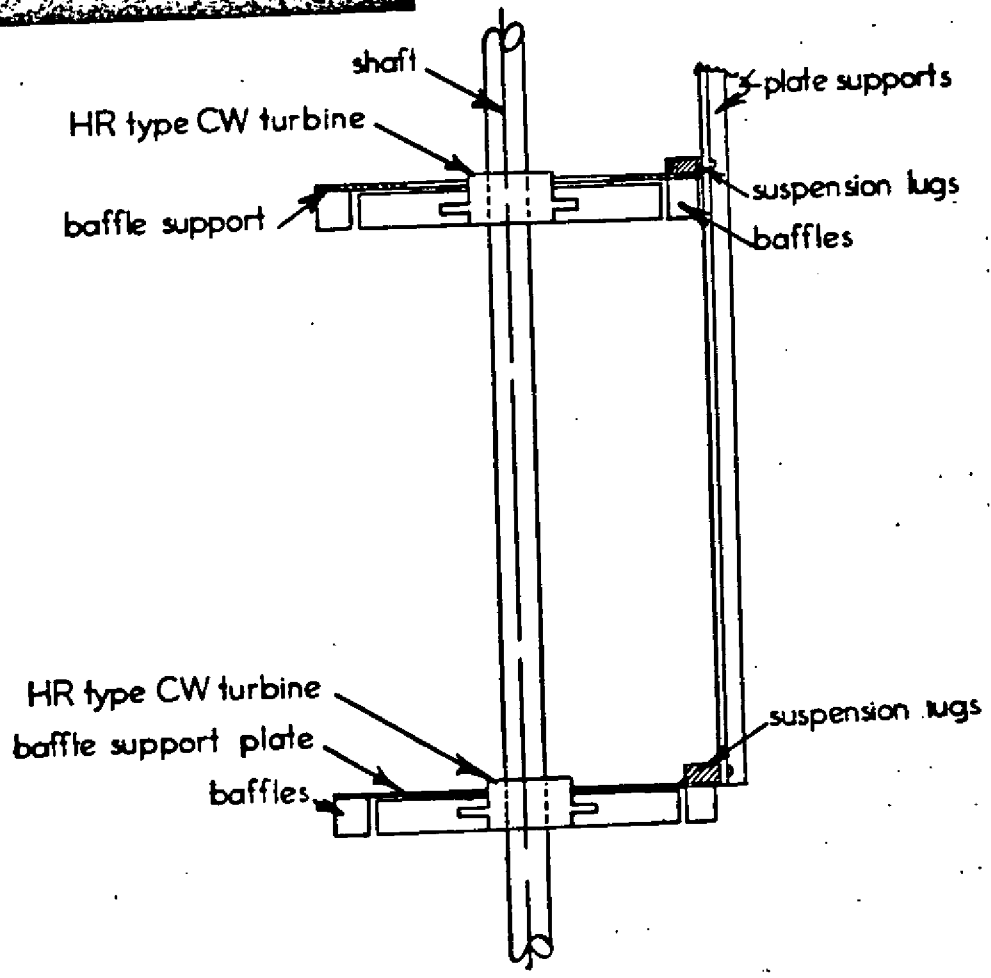


Fig. 7: Hendrick Normal Turbine Mixer in Multi-Turbine arrangement

Dissolving problems in which the [illegible]ed solids do not take on a jelly-like consistency upon solvent infiltration.

The agitation of blends or mixtures in which readily miscible components are a characteristic. Agitation in reaction vessels in which maximum rates of heat transfer are the prime consideration and in which contact between the reactants is accomplished as a function of ready miscibility or solubility of reactants in one another.

By special mechanical adaptation, the dispersion of gases in liquids in which the contacting problem is not critical or in which small quantities and rates of gas dispersion are involved.

The Hendrick Normal Turbine excels propeller type mixers in that:

the efficient functioning of the Normal Turbine is not as critically dependent upon ideal kettle shape and design as in the case of propeller mixers;

the maintenance of uniform efficiency of mixing is not contingent upon the maintenance of uniform "mix" consistency throughout the mixing operation;

the Normal Turbine maintains a center-to-periphery exchange of materials as well as a vertical interchange, as opposed to the simple thrust action of propellers.

The Normal Turbine in operation (Fig. 8) acts to draw the tank liquid toward itself in the vicinity of its hub, expelling the liquid over its entire periphery in a tangential direction to any point on the periphery. In the cases of low viscosity liquids, the tangential delivery of the rotor, under ordinary conditions, would tend to develop an excessive swirling action. This is prevented by one of two modifications of the basic Normal Turbine design; the addition to the turbine of a radial baffle assembly; the shrouding of the turbine. The friction of the batch on the tank wall is, in the instance of moderate to high consistency liquids, sufficient to prevent wasteful swirling in the liquid mass.

For certain applications, Hendrick Normal Turbine assemblies, special baffle assemblies or special draft-tube arrangements are desirable. Certain shapes of tanks demand multi-turbine assemblies to insure the uniform agitation of the vessel's contents. If you will submit your mixing problem to us, we shall be glad to work out with you that adaptation of the Normal Turbine assembly best suited to your requirements.

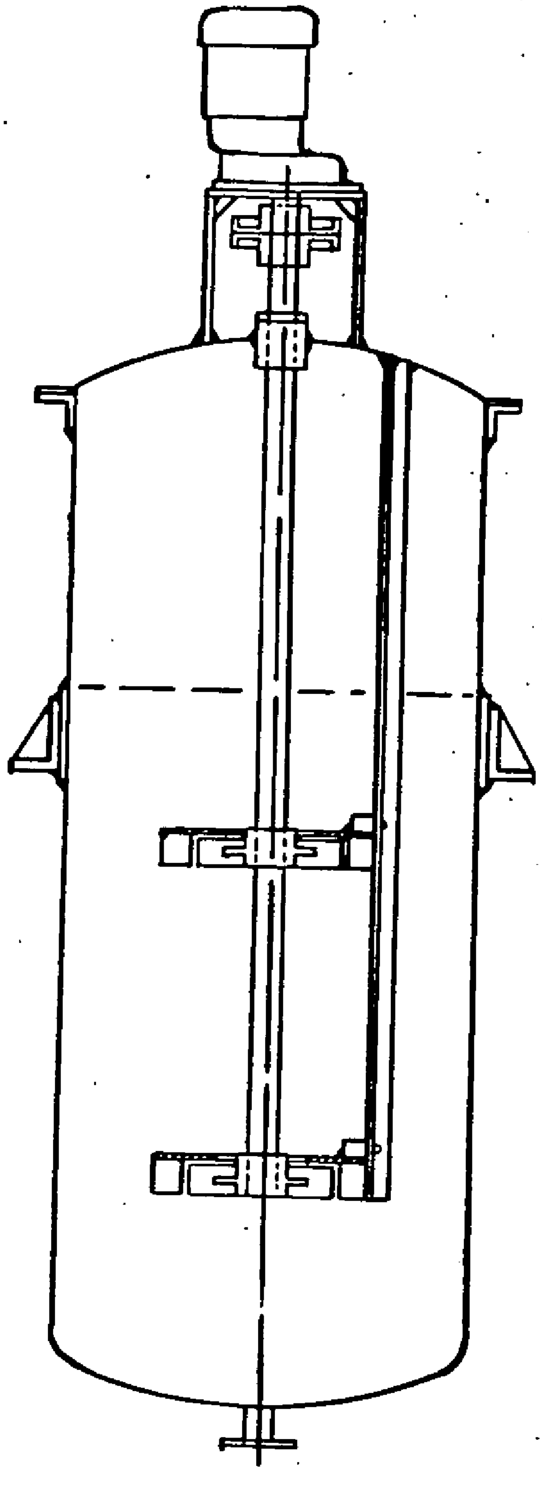


Fig. 8. Hendrick Multi-Turbine assembly in slender-shaped reaction vessel.

Hendrick Paddle, Gate, Horseshoe, Anchor Mixers

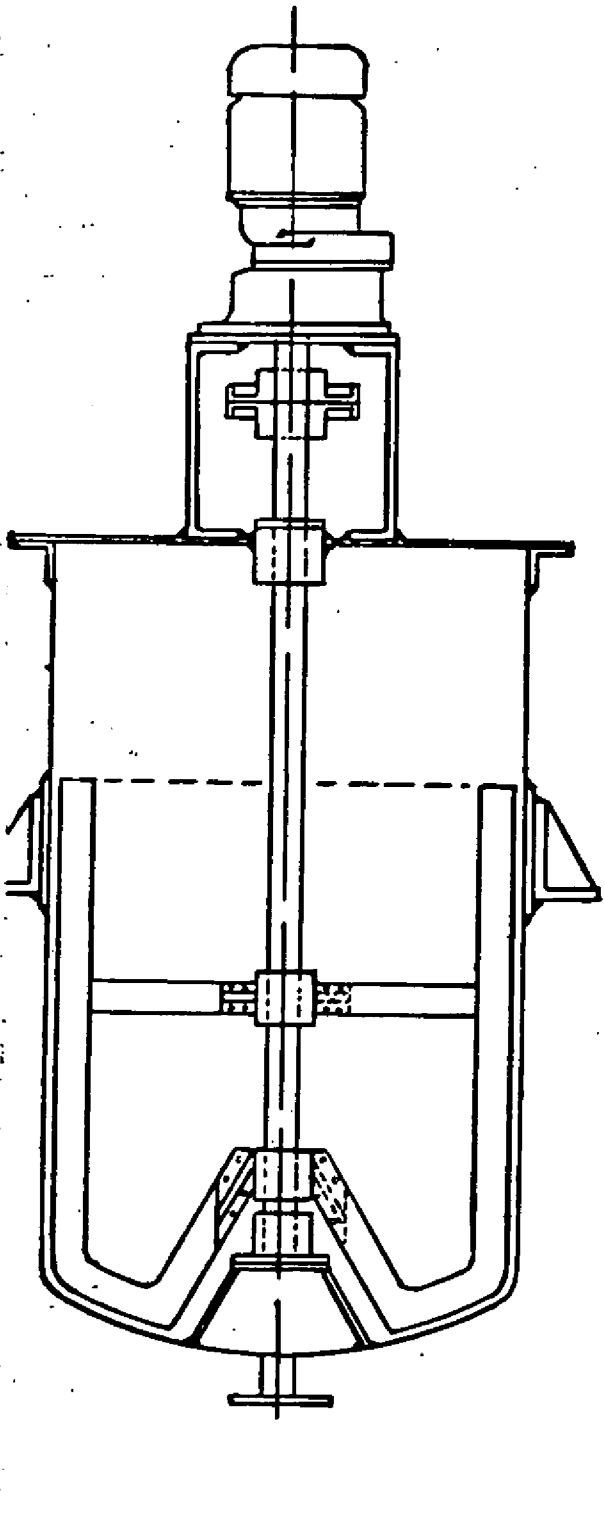


Fig. 9. Hendrick Horseshoe Mixer, bolted type.

Hendrick Paddle, (Fig. 10) Gate, Horseshoe (Fig. 9) and Anchor Mixers, by reason of the wide possible lattitude in design arrangements and because of the speed ranges employed, are well suited to:

Mixing operations involving a "mix" characterized by an inverted plasticity.

Solid-liquid mixing operations in which severe turbulence or mechanical abrasion of the suspended solids is objectionable as in the agitation of certain pulp slurries.

Operations involving at any time during the mixing cycle a product having a viscosity exceeding 50,000 to 60,000 centipoises.

The agitation of slurries having extraordinarily high dry contents and poor flow properties.

Hendrick Paddle, Gate, Horseshoe, and Anchor Mixer Assemblies may be furnished for all shapes and sizes of tanks. They are designed to meet, from the standpoint of type, spacing and speed, the specific service conditions obtaining in each problem. These mixer assemblies are available in two basic types: bolted, "knockdown" assemblies; all-welded construction.

Gate and Horseshoe agitators may be supplied with scraper or edge-running devices (Fig. 11), depending upon wall-cleaning requirements.

Hendrick Engineers will gladly submit proposals and drawings covering double-action combinations such as gate-and-turbine or paddle-and-gate combinations.

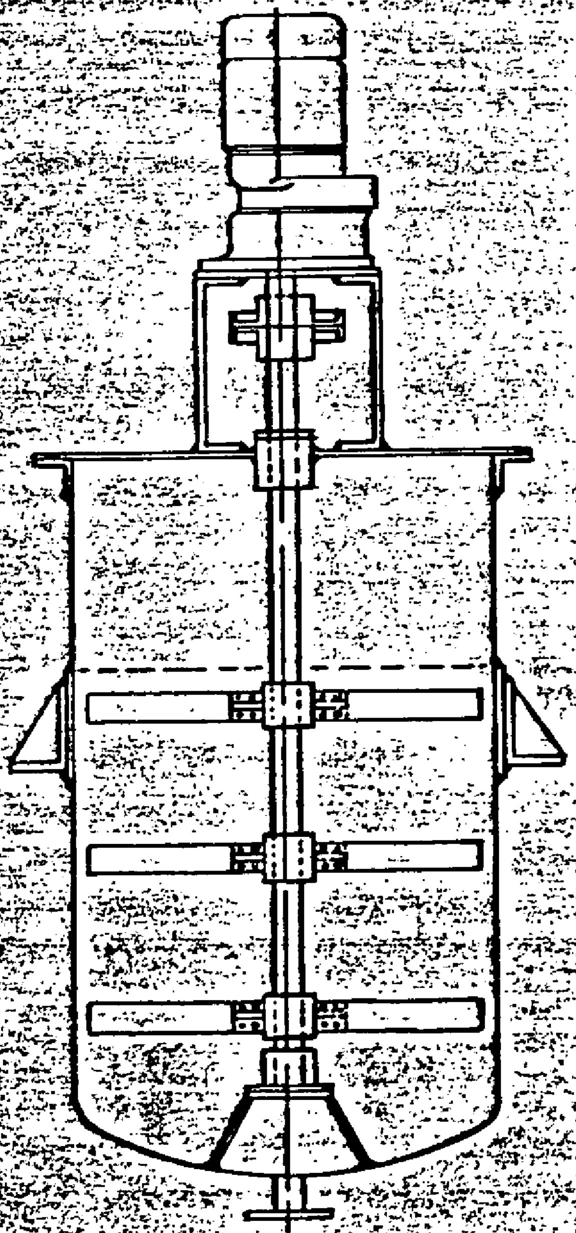


Fig. 10. Hendrick Paddle Mixer in stock chest.

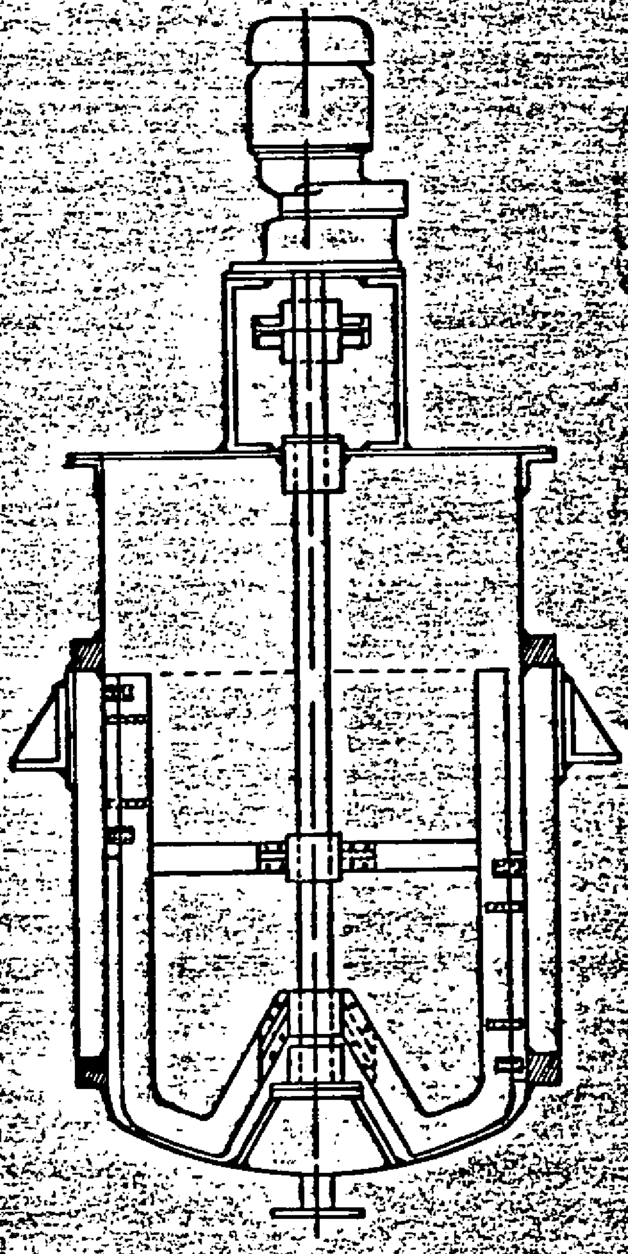


Fig. 11. Hendrick Horseshoe and Scraper Assembly in tank for thinning and cooling hot pitch.