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LACHRYMATORS

PART II

ACROLEIN.

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[redacted]

FOREWORD

Because of the large number of substances which have been studied for their possible use as lachrymators, it has been thought best to issue the monograph on this subject in parts.

Part I will consist of a general discussion of the question and of the methods used in their study. The following parts will discuss the various compounds in detail. These will be issued at irregular intervals as pressure of other work permits. A collective index will be issued at the end of the series.

Clarence J. West.

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LACHRYMATORS

PART II

ACROLEIN.

$CH_2 = CHCHO$

INTRODUCTION

British investigators report that crude acrolein (containing 25% ether) was quite ineffective as a lachrymator.

The pure acrolein attacks the eyes and throat, but the vapors are too light. The addition of CCl_4 or $C_2H_4Cl_4$ gave no better results.

It has been suggested that the acrolein should be generated *in situ* in the shells. This is not feasible, because acrolein can be prepared only from glycerol, of which there is a shortage at present.

The French have found that while acrolein is effective in clearing dugouts it is not as effective as stannic chlorid which is used for the same purpose.

The Offensive Warfare Committee of the Division of Offensive Chemical Research, Feb. 21, 1918, considered the work on acrolein and decided that the preparation of this compound had been so thoroughly investigated that no further laboratory work on this problem was necessary. Whether this substance should be manufactured or not would seem to depend on the availability of the raw material -either glycerol or trimethylene glycol (B.M. XIII-47).

I

PREPARATION

Owing to the pressure of other work no attempt will be made here to collect all the data on the preparation of acrolein. Only that which has been carried out by workers connected with the Research Station will be included. However, a complete bibliography (compiled by L. H. Flett, Mass. Inst. Tech.) is given at the close of the chapter for those who desire further information.

The preparation of acrolein is generally carried out by the dehydration of glycerol. The problems are the choice of a suitable catalyzer and proper temperature conditions.

Magnesium Sulfate as Catalyzer.

The most suitable method for the preparation of acrolein seems to be that of Wohl and Mylo (Ber. 45, 2046 (1912). It consists in passing glycerol vapors through an electrically heated column packed with a catalyzing dehydrating material, carefully maintained at a definite temperature, and removal of water and other by-products

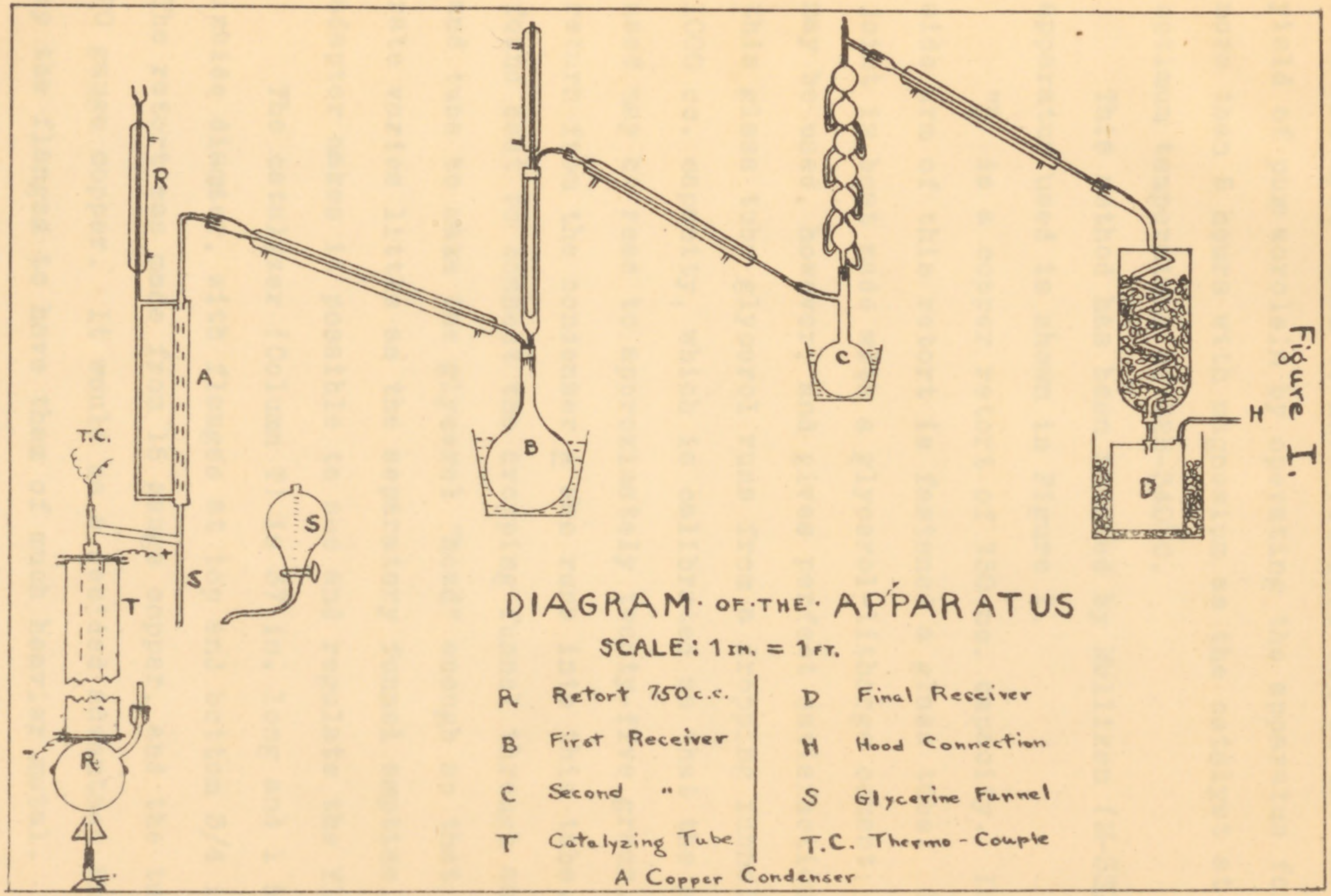


Figure I.

DIAGRAM · OF · THE · APPARATUS

SCALE: 1 IN. = 1 FT.

R Retort 750 c.c.
B First Receiver
C Second "
T Catalyzing Tube
D Final Receiver
H Hood Connection
S Glycerine Funnel
T.C. Thermo-Couple
A Copper Condenser

PLATE I

by a well controlled fractional distillation and condensatior Wohl and Mylo claim to have obtained 60% of the theoretical yield of pure acrolein by operating the apparatus for not more than 5 hours with magnesium as the catalyst at the optimum temperature of 325-340°C.

This method has been studied by Mulliken (M-331). The apparatus used is shown in Figure I.

"R is a copper retort of 750 cc. capacity. Into the side arm of this retort is fastened a glass tube. This joint is best made with a glycerol-litharge cement; a cork may be used, however, and gives perfect satisfaction. Into this glass tube glycerol runs from a dropping funnel S of 1000 cc. capacity, which is calibrated so that the glycerol used may be read to approximately twenty-five grams. The return from the condenser A also runs into this tube. It is found best to connect the dropping funnel through an adapter and tube to make the glycerol "head" enough so that the rate varies little as the separatory funnel empties, and the adapter makes it possible to see and regulate the flow.

The catalyzer (Column T) is 37 in. long and 1 5/8 in. inside diamter, with flanges at top and bottom 3/4 in. wide. The retort was made from 16 gauge copper, and the tube from 20 gauge copper. It would be a decided advantage in making up the flanges to have them of much heavier metal. The lower joint was made up with packing and six bolts. The upper joint was first made in the same way but later small steel clamps were used. For packing Johns-Mansville's

"Kearsage" was used, and also graphitized packing. Water glass aids in making the joints tight.

The catalyzer tube is wound first with thin asbestos paper and then with 25 feet of nichrome ribbon 0.100" x .012", of resistance .42 Ohms per foot. This is held in place by alundum cement, which was mixed with water and brushed on, and the whole covered with magnesia steam pipe covering. Direct current is used for heating, about 4 amperes and 47 volts giving the desired temperature.

The temperature of the tube was first measured by a copper-"Ideal" thermo couple and "potentiometer." The junctions were silver soldered. The hot junction was placed in a glass tube and this was placed in an iron tube extending to near the bottom of the column. It was kept in the hottest part of the tube near its middle which we found to be fairly uniform in temperature. Later the temperature was taken by hanging a thin thermometer in the iron tube and this gave results nearly as satisfactory.

<u>A</u> is a copper condenser connected by copper tubes to the catalyzer column. It is designed to return unchanged glycerol. The jacket was filled with boiling toluol which in turn was retained by a reflux condenser, R.

The crude acrolein vapours are condensed in an ordinary glass condenser and run into flask B of 2000 cc. capacity. From this crude acrolein is obtained by use of a modified Hahn (Ber. 43, 422) column. It is condensed and passes into a 500 cc. side arm flask C, from which it is fractione by means of a Le Bel-Henniger column. The vapors are condensed by an iced worm in the receiver D which is also packed in ice. A Woulff bottle or a filtering bottle serve well as receivers. Any escaping gases are conducted to the hood by means of glass and rubber tubing.

The catalyzer is supported in the tube by means of a disk of copper gauze of about 4 mesh which is just too large for the entrance to the retort.

The retort is heated by means of a Tirrell burner with the flame about six inches high and the inner cone visible.

The heating baths are filled with cottonseed oil and are heated by gas or electricity. B is kept at 120°C. C is kept 90° - 110°C. Column B is about 90°C. F is about 60°C."

Results obtained by this method are given in the following table:

Comparison of Runs made with 99% Glycerol and Magnesium Sulphate Catalyzer

No. of Run	Time in Hrs.	Grams 99% Glyc.	Rate Glycerol: Grams p. Hr.	Yield %* Theory	Average Temp. Tube	Max Temp. Tube
2	3.5	900	257	35	302 --18.7	332°
3	10	2600	260	39	325 --13.0	350°
4	15	3685	246	37	318 -- 5.8	331°
5	13	2850	219	35	320 -- 6.5	328°
6	20	4120	206	50	328 -- 4.9	334°
8	16	2790	175	36	322 -- 6.5	335°
9**	15	2950	200	51	346 -- 5.1	355°
10	9	3600	289	40	332 -- 8.0	346°
12	14	2400	172	43	344 -- 5.0	350°
13	15	3000	200	46	335 -- 0.0	340°

* These yields are uncorrected for the glycerol which distilled over into flask B unchanged. This liquid was found to contain about 25% glycerine. Correcting the above yields for this, our maximum yield is a little over 61%.

**Specific gravity #9; first 910 grams. = 0.854 at 15.5°; last 450 g., 0.857 at 18°.

Catalyzer- The crystallized magnesium sulfate was dehydrated by heating in an iron pan. A vigorous evolution of steam left a firm porous cake, which was broken up into bean-sized fragments before packing in the tube.

After using, the catalyzer had a reddish brown color. The lump did not seem to disintegrate. Fracture showed that the pieces were of almost uniform color throughout except for thin incrustations of black tar in some parts of the column.

The yield of acrolein decreases after the catalyst has been used for a few hours. The falling off in efficiency after 5 or 10 hours was marked. There is no doubt, however, that a properly jacketed and carefully operated apparatus may be run continuously with advantage for many hours.

Temperature.- The best yields of acrolein were obtained at temperatures between 328-346°, and with an average flow of glycerol of about 200 gm. per hour. The temperature has to be controlled accurately. Wohl and Mylo state that at this temperature more than half of the glycerol is transformed into acrolein, while slightly higher temperatures favor the production of β-hydroxypropionaldehyde or hydroxyacetone, according as the primary or the secondary hydroxyl group is attacked. The hydroxyacetone at once decomposes into acetaldehyde and formaldehyde. The rate of feeding must also be controlled.

Kohler used a simpler apparatus. No yields are given.

The apparatus consists of a copper tower about three feet high and four inches internal diameter, filled with lumps of anhydrous magnesium sulfate. This tower was connected in a vertical position to the mouth of a copper flask (about one liter capacity). The other end of the tower was connected to a glass condenser. Glycerol was bailed in the flask; the vapors passed up through the magnesium sulfate, where they were largely changed into acrolein. The gases issuing from the mouth of the cylinder were condensed fractionally and the final condensation fraction was purified by distillation. This product contains from 10-20% acetaldehyde, which cannot be conveniently removed.

The acrolein obtained by this process (Mulliken) was always a yellowish product containing water and acetaldehyde.

It was, however, free from sulfur dioxide.

Magnesium pyrophosphate as Catalyzer.

The apparatus employed was that described above.

The magnesium pyrophosphate was made by strongly igniting magnesium ammonium orthophosphate in a muffle furnace. The powdered pyrophosphate was moistened with about 2% of syrupy phosphoric acid diluted with water, and the slightly damp mass compressed to cupels in a cupel mould of the type used in furnace essay work. The cupels were then broken into bean-sized pieces, and dried at 100°C. The pieces were then hard stony lumps.

The following table shows the results obtained from the use of magnesium pyrophosphate:

Runs with Mg_2P207

Run No.	Length of run	Temp. Tube	Grs. Glycerine used	Rate Glycerine (g. per hr.	Yield of Acrolein Uncor. (B.P. 51-53°
18	2½	326°C	1050	420	47%
18a	18	315	5275	292	29%
29	2	320	1010	505	52%
2929a	5	325	1610	302	49%

The acrolein prepared by this method was remarkable for its purity, freedom from color, and comparatively excellent keeping qualities. When slowly distilled through a Le-Bel-Henninger column nothing boiling below 51° was condensed, and acetaldehyde was apparently wholly absent. If a correction were to be made for the unchanged glyercol recoverable from flask B, the yields of pure acrolein would become fully 60% of the theoretical.

One of the most striking facts connected with the use of the pyrophosphate is the high acceleration which it induces in the dehydrating reaction. The reaction if conducted at a temperature of 325°C. will transform about twice as much glycerol into acrolein in a given time as with magnesium sulphate, and the condensate in the recipient D remains practically colorless to the last. The most serious drawback to the use of pyrophosphate is its short life as a catalyst. The black asphaltic tars forms much more rapidly than with other catalysts, and in the small apparatus used chokes the upper layers of the column and the exit tube after a few hours. It is as tenacious as hard asphalt and difficult to remove after hardening. The product from Run 29, which was stored in a closed closet in a bottle containing a small reduced copper gauze spiral, remained clear, colorless, and mobile two and a half months after preparation, although it had been opened and shaken many times in the interim. At the end of three months, (when last observed) the separation of a white precipitate was just beginning.

Preparation of Acrolein with Bone-ash Catalysts.

It was thought possible that bone-ash cupels made by moistening the ash with enough dilute sulphuric or phosphoric acid to give the mixture a slight acidity by formation of acid calcium phosphate might give results similar to those obtained with the acidified magnesium pyrophosphate, and prove an economical substitute for this material. Bone ash without acidification is very inactive.

In these experiments the cupels were mixed, compressed, and dried in the same general way as the magnesium pyrophosphate mass. The glycerol used (a 98% dynamite glycerin), and the apparatus, were also the same in both series of experiments.

The following table shows the data secured in the bone-ash runs.

In Runs #19 and #20 the cupels were moistened with phosphoric instead of sulphuric acid. The products showed less tendency to polymerize than those from experiments in which sulphuric acid was used, but an unusually heavy deposit of tenacious black tar accumulated and finally choked up the central part of the catalyzer column.

The apparatus functioned most smoothly in Runs Nos. 22 and 23 in which the bone ash was moistened with 15% of sulfuric acid. The clogging and tar formation was perhaps a little more troublesome than in runs with magnesium sulphate, but the conversion was more rapid and the product was much lower in acetaldehyde. Not more than about 100 drops of distillate boiling below 51° were collected from any one of the crude products when slowly distilled through a 6-bulb LeBel-Henninger column. Increase of the proportion of sulphuric acid to 20% increases the tar, difficulty in

Results with Bone-Ash Catalysts

Run No.	Catalyst	Length of run. Temp. of Catalyst	Glycerine used (in grs)	Yield in Acrolein in grams	Yield in Acrolein in% of theory	Yield in Acrolein in% when corrected*	Sp.Gr. of Product at 15°.	Boiling Point of Product	Remarks
19	Bone ash +11%H_3PO_4	10½ hrs. 303-317°	1700	333	32.5	----	0.850	51-54°	Products of good stability. Much tar on catalyst.
20	Bone ash +5%H_3PO_4	320-325°	1190	225	32.5	40.5	0.847	51-54°	
23	Bone ash +15%H_2SO_4	8 hrs. 315-339°	1785	531	50.8	62.6	0.848	52-53°	Products of moderate stability. Considerable tar on catalyst
22	Bone ash +15%H_2SO_4	9½ hrs. 320-330°	1600	477	51.0	60	0.846	51-53°	
24	Bone ash +20%H_2SO_4	7½ hrs. 320-330°	1100	180	28.1	39.6	0.850	51.53°	Products very instable. Much tar on catalyst. Run 24 very irregular.
25	Bone ash +20%H_2SO_4	2½ hrs. 320-330°	890	250	48.3	----	0.852	51-53°	
26	Bone ash +10%H_2SO_4	9½ hrs. 315-325°	1940	418	37.0	51.2	0.852	51-53°	Products of Moderate stability. Little tar in catalyst
27	Bone ash +10%H_2SO_4	9 hrs. 325-340°	2020	495	42.6	58.2	0.852	50-54°	

*Yield corrected for recoverable glycerine accumulating in Flask B regular operation and leads to more unstable products. Thus the product of Run 24 polymerized to a solid glassy mass (although in contact with copper) within a month, while its duplicate No.25 gave a product that began to polymerize within a few hours. (See Page

Aluminium Salts as Catalyzer.

Experiments with aluminium phosphate and aluminium sulfate as catalysts were very unpromising (Mulliken). Engelder (B.M. IX-21, XII-32) found that aluminium oxide gave as good results as magnesium sulfate, the yields of acrolein running from 19 to 36%. Al_2O_3 yields a smaller amount of by-product (acetaldehyde and formaldehyde) than the other catalysts and the undecomposed glycerol can be recovered.

Evans has made (B.M.III-20) a comparative study of various catalysts in the preparation of acrolein with the following result;

CATALYST Gm.	GLYCEROL Gm.	ACROLEIN	
		Crude	Pure
$KHSO_4$ -- K_2SO_4 500 gm.-150	220	50%	36.5%
$KHSO_4$ K_2SO_4 1000 gm.-250	500	73.3	36.7
$K_2S_2O_7$ -- K_2SO_4 1000 gm.-300	440	73.3	52.5
$MgSO_4$ 160	755	40.0	34.2
KPO_3 - HPO_3 118 gm.- 80	150	45	
$Na_2P_2O_7$ -- H_3PO_4 113 gm.-115	150	35.5	
$AlPO_4$ - 122	200	18	
$Mg_2P_2O_7$ - 160	100	12	

Evans believes that a considerable percentage of the product obtained by means of the more familiar methods is acetaldehyde and other impurities.

BY-PRODUCTS IN PREPARATION OF ACROLEIN WITH THE WOHL MYLO APPARATUS

Although porous carbon may form in large quantities in the copper flask if the glycerol level be allowed to fall too low so that the metal of the side walls becomes overheated, the loss from carbonization in most experiments was very small. The loss from the formation of black asphaltic deposits on the catalyst mass was a factor of more importance when acid phosphates were employed, but was not considerable in the experiments with the magnesium sulphate or the faintly acidified bone-ash catalysts. In experiments with magnesium sulphate, even at the lower temperatures, the loss through formation of free acetic aldehyde was found greater than Wohl's paper had led us to anticipate, and it is probable that the contents of Flask B̲ may have contained appreciable quantities of condensation products of acetic and formic aldehyde. When using the acid phosphates, on the contrary, the condensate in recipient D̲ was free from acetaldehyde. The small condensate remaining in Flask C̲ at the close of runs rarely exceeded 50 cc. and consisted of a brownish pungent oily mixture and water. It is now probable that it consisted in part of some of the compounds isolated by Prof. Moureu from the French "Papite" and described in Z-124. Small quantities of oils of similar appearance sometimes separated from the aqueous solutions in Flask B̲, or were obtained as small layers separating from aqueous condensates when these solutions were distilled long enough to drive over most of their water.

The greater part of the glycerol not converted into acrolein by passage through the Wohl-Mylo apparatus, that could be definitely accounted for, was found in the contents of Flask B̲. This dark-colored solution presumably contained some of the aldehydic condensation products mentioned in the "Notes on the Mechanism of the Reaction for the Preparation of Acrolein from Glycerol" by L. H. Flett which is given below, along with traces of the aromatic oils mentioned in the last paragraph. But it behaved on distillation almost exactly like an aqueous crude glycerol solution of the same specific gravity, as was well established by a comparison of its distillation curves, showing boiling point temperatures plotted against volumes, with similar curves obtained from distillation experiments made in the same flask in which glycerol solutions of the same gravities were distilled to dryness at the same rate. This conclusion was verified by concentrating the residues in Flask B to a gravity corresponding to an 80% glycerol and using the concentrates for regular runs for acrolein in the Wohl-Mylo apparatus. The acrolein yields were only a little lower than those in experiments with 80% glycerol.

The following table shows the yields of acrolein actually obtained in certain runs, and the yields that would have been obtained if the glycerol in Flask B (calculated from specific gravity) had been all recovered as such. Obviously the composition of the solution in Flask B would not be exactly the same in different experiments unless the conditions of operation were identical, and any change in the design of the fractional condenser A would be likely to have an influence upon it.

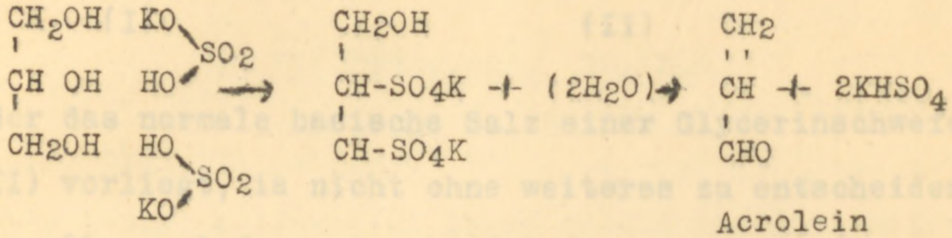
TABLE SHOWING YIELDS OF ACROLEIN FROM CERTAIN RUNS BEFORE AND AFTER CORRECTION FOR GLYCEROL COLLECTED IN FLASK B.

Run No.	Amount of glycerol used in grams	Acrolein Yield			Liquid in Flask B*		
		Grams	Actual Yield in % of theory	Yield after correction for Flask B	Grams	Spec. Grav.	% Glycerol from Sp.Gr.
20	1200	225	32.5	40.5	710	1.083	33
22	1400	477	51.0	60.	745	1.066	26
23	1790	531	50.8	62.5	995	1.084	33
24	1100	180	28.1	39.6	772	1.106	42
25	890	250	48.3		553	1.091	36
26	1950	418	37.0	51.2	1220	1.110	43
27	2020	495	42.6	58.2	1200	1.120	44
29	1600	333	49.0		650	1.173	45.5
30	1600	305	32.6		1074	1.102	40

THE MECHANISM OF THE REACTION FOR THE PREPARATION OF ACROLEIN FROM GLYCEROL

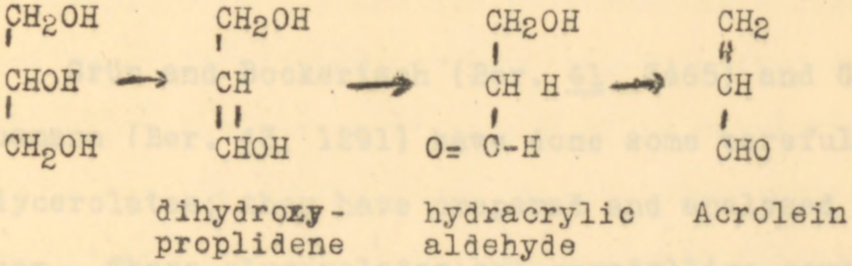
The following discussion was written by L. H. Flett.

Acrolein. It was observed by Hübner and Geuther (Ann. 114, 35) that, in the distillation of glycerol with potassium acid sulfate only water was given off at first. When this stopped an increase of temperature was necessary for the evolution of acrolein. They concluded that a glycerol potassium sulfate was formed, with an evolution of water, which broke up at a higher temperature with the evolution of acrolein. Senderens (Bull. Soc. Chem. 9, 374) gives the reaction--



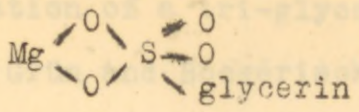
The sulfate is then available for further action.

Nef (Ann. 335, 207) after some careful research gives the reaction as follows--

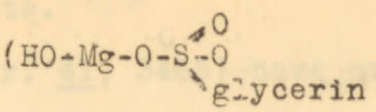


Wohl and Mylo (Ber. 45, 2048) suggest Nef's reaction but say "Für das von ihm formulierte auftreten von Methylene Verbindungen (mit zweiwertigen Kohenstaff) als Zwischenprodukten fehlte aber eine experimentelle Begründung wahrend die Bildung von Ketonen and Aldehyden als intermediär enstanden Enolen durch zahlreiche Erfahrung gestützt wird."

As to the part the catalyzer plays, Wohl and Mylo say, "Ob hier ein Additionproduct der Zusammensetzung (I)



(I)



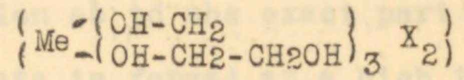
$(HO{-}Mg{-}O{-}S\begin{smallmatrix}\nearrow O\\ -O\\ \searrow \text{glycerin}\end{smallmatrix}$

(II)

oder das normale basische Salz einer Glycerinschwefelsaure (II) vorliegt, is nicht ohne weiteres zu entscheiden.

Glycerol forms two kinds of compounds with inorganic compounds, the glycerates, such as $C_3H_5(OH)O_2Ca$ and the glycerolates, of the general formula:

$(Me3C_3H_5OH_3)X_2$ or

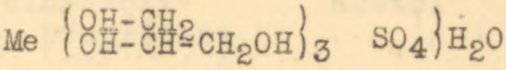


$$\left(Me\begin{smallmatrix}\nearrow\\ \searrow\end{smallmatrix}\left(\begin{matrix}OH\text{-}CH_2\\ OH\text{-}CH2\text{-}CH2OH\end{matrix}\right)_3 X_2\right)$$

Grün and Bockerisch (Ber. 41, 3465) and Grün and Husmann (Ber. 43, 1291) have done some careful work on the glycerolates; they have prepared and analysed several of them. These glycerolates are crystalline compounds and intensely hydroscopic. They are very stable, as would be expected from the five-membered cyclic formation. By heating, glycerol is evolved unchanged but by heating with a dehydrating agent acrolein is formed. The addition of glycerol appears to be independent of the ability of the salt to add water.

Grün and Husmann (Ber. 43, 1293) noticed that in working with lime acrolein was formed. They subsequently distilled glycerol from calcium hydroxide and obtained only 1.7% acrolein. This would show that there is little tendency for the formation of acrolein as a result of the formation of a tri-glycerolate.

Grün and Bockerisch (Ber. 41, 3465) have prepared the compounds--



$$Me\left\{\begin{matrix}OH-CH_2\\ CH-CH=CH_2OH\end{matrix}\right)_3 \quad SO_4\Big\}H_2O$$

Me = Co, Ni, Zn, Cu.

In the normal sulfates of these metals the last water molecule is the hardest to separate so it appears in the glycerolate. Cations of the form $(Me3(C_3H_5(OH))_2)^{++}$ are also believed to form in some cases.

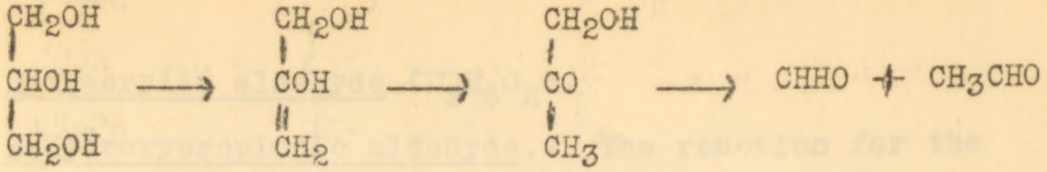
There is no information as to the exact part of the catalyzer. If a glycerolate is formed at a high temperature there is still a question as to the formation of acrolein. Certainly a dehydrator of some kind is necessary as can be seen in the low yields given by substances which do not form hydrates. The information suggests the advisability of using a catalyzer, i.e., a glycerolate-forming salt and a dehydrator such as a bisulfate or pyrosulfate.

Almost any treatment of glycerol yields acrolein in variable quantities so the action of catalyzers yielding small results will not be considered, although some. in particular the acids, certainly must form intermediate compounds.

Intermediate and Decomposition Products.

Acetol.- Acetylcarbinal-CH_3-CO-CH_2OH-(Beilstein I, 267)

Acetol is the most important decomposition product of glycer outside of hydracrylic aldehyde and acrolein. It breaks up i to formaldehyde and acetaldehyde. Nef(Ann.335,221) gives the reaction-



$$\begin{matrix} CH_2OH & & CH_2OH & & CH_2OH & & \\ | & & | & & | & & \\ CHOH & \longrightarrow & COH & \longrightarrow & CO & \longrightarrow & CHHO + CH_3CHO \\ | & & \| & & | & & \\ CH_2OH & & CH_2 & & CH_3 & & \end{matrix}$$

dihydroxy-propilidene acetol

The above remarks about methylene dissociation should still be borne in mind.

Acetol is highly undesirable. Its dissociation represents glycerol losses. It condenses easily and is believed to be responsible for the tarring of the catalyzer. It boils at 147o not undecomposed and so would certainly not pass beyond the first flask, Figure 1. It is undoubtedly all held in the first column as tar.

Acetol combines at 100° with two mols. of phenylhydrazine to form methylglyoxal osazone.

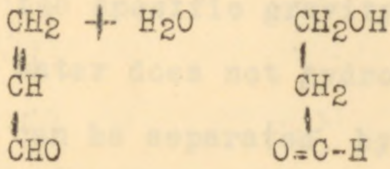
There is no reason to assert that the acetaldehyde in the product is a fair measure of the acetol formed, but this much can be said, that if it is, then the amount of acetol varies with the catalyzer. Wohl and Mylo (Ber. 45, 2046) assert that it varies with the temperature, the formation of acrolein being favored by low temperatures.

<u>Formaldehyde</u>.- Formaldehyde comes from acetol and probably from hydracrylic aldehyde. What does not polymerize to form formaldehyde-glycerol passes out the condenser, carrying with it acrolein vapors.

<u>Acetaldehyde</u>.- The source is the same as formaldehyde. It forms acetaldehyde-glycerol. It is the chief impurity of the acrolein.

Hydracrylic aldehyde ($C_3H_6O_2$).

B-Hydroxypropionic aldehyde.- The reaction for the dissociation of hydracrylic aldehyde is reversible. If water and acrolein are kept at 100° for some time they combine forming hydracrylic aldehyde.

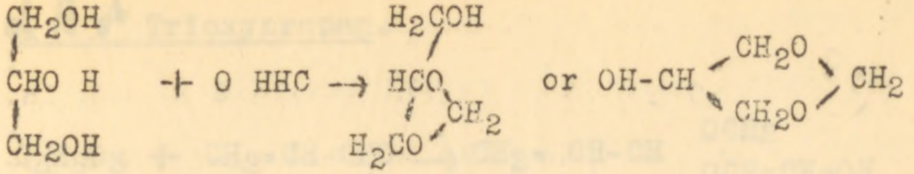


$$\begin{array}{lll} \mathrm{CH_2} + \mathrm{H_2O} & & \mathrm{CH_2OH} \\ \| & & | \\ \mathrm{CH} & & \mathrm{CH_2} \\ | & & | \\ \mathrm{CHO} & & \mathrm{O{=}C{-}H} \end{array}$$

Acrolein

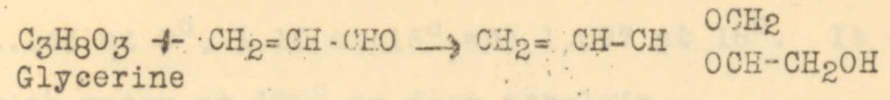
It was first prepared and analysed by Nef (Ann. 335, 219). It is a liquid of B.P. 90° at 18 mm. It has a sharp smell. It condenses easily and polymerises some. Its semicarbazone melts at 140°. Nef (Ann. 335, 220). It reduces ammoniacal silver nitrate, but not Fehlings's solution. It is easily soluble in water but difficultly soluble in ether. A.Wohl prepared it from oxyacetal (Ber. 41, 3603) and describes it as soluble in ether and difficultly soluble in water. Hydracrylic aldehyde probably exists in the catalyzer tube and in the first and second flasks. It can be decomposed by heating it from 140° - 200° with potassium bisulfate (Nef, Ann. 335, 221).

Formaldehyde-glycerine ($C_4H_8O_3$); monoformal methyleneether.- (Beilstein I. 468;Schulz and Tollens (Ber. 27, 1894) obtained this product by heating together formaldehyde and glycerol. It has two isomeric modifications. One gives a crystalline and one an oily benzoate.



It is easily formed at 100°. Its boiling point is 193° (197°); the specific gravity is 1.205 at 20°. Continued heating with water does not hydrolyse it. It is soluble in water and can be separated, by adding potassium carbonate, with ether. This should occur in considerable amounts in the first flask only. Glycerol formal benzoate is formed by adding sodium hydroxide and benzoyl chloride, M.P. 72°. Acetaldehyde-glycerol ($C_5H_{10}O_3$); Ethylidine; αβγ Tri-oxypropane; Acetoglyceral. (Beilstein I,924).- This is formed by letting acetaldehyde react with glycerol. It is a liquid of boiling point 85°-87° at 18 mm, 184-188° at 760 mm. and specific gravity 1.118. It is easily soluble in cold water and is decomposed by heating to 100° with ten parts of water. It does not reduce Fehlings solution. For all that it may be easily decomposed by boiling with water, Nef found it as the chief member of this series of glycerol compounds. (Ann. 335, 214). It should be found in the first flask in appreciable quantities.

α-Acrolein-glycerol ($C_6H_{10}O_3$); αβ Ethylidinether; αβγ Trioxypropan.



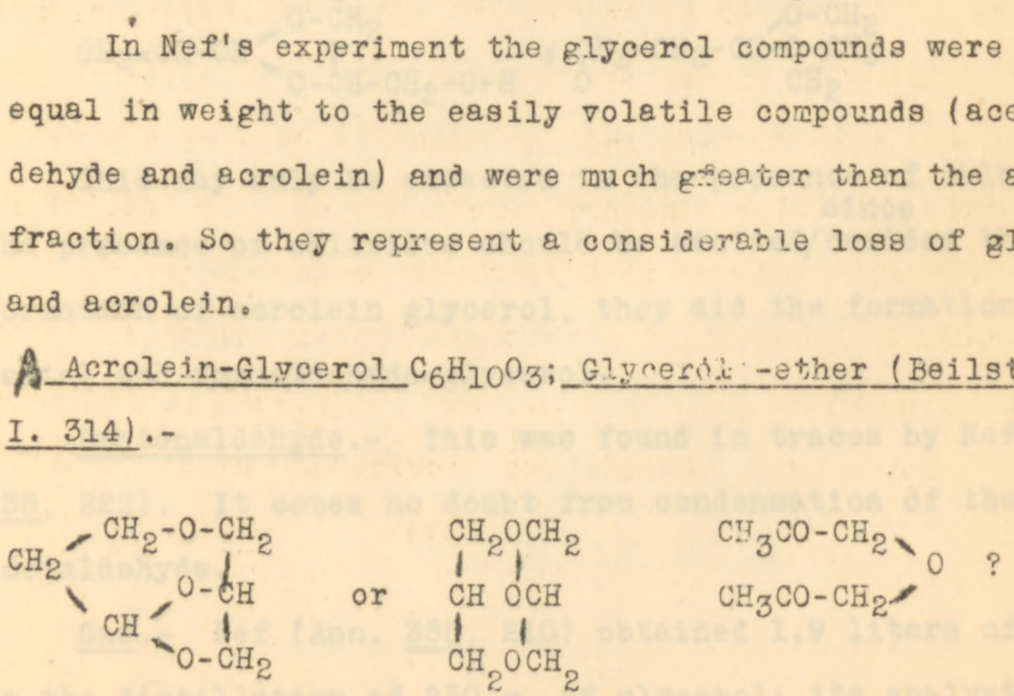
$$\underset{\text{Glycerine}}{C_3H_8O_3} + CH_2{=}CH{-}CHO \longrightarrow CH_2{=}CH{-}CH\begin{matrix}OCH_2\\OCH{-}CH_2OH\end{matrix}$$

α Acrolein-glycerol

This product has not been analyzed. Nef, (Ann. <u>335</u>, 216) prepared a very impure product which boiled at 102°-106° at 17 mm. The reversibility of the reaction and the reaction between acrolein and water made a pure product impossible. The compound is hydrolysed by heating six hours with ten volumes of water at 100°. In spite of its tendency to hydrolyze, Nef (Ann. <u>335</u>, 210) found appreciable amounts of it in the decomposition of glycerol. It should be found up to the first flask only.

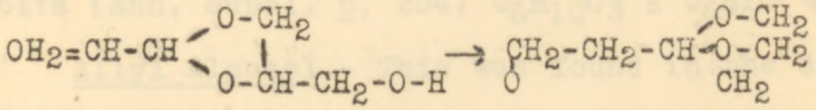
In Nef's experiment the glycerol compounds were almost equal in weight to the easily volatile compounds (acetaldehyde and acrolein) and were much greater than the acetol fraction. So they represent a considerable loss of glycerol and acrolein.

β Acrolein-Glycerol $C_6H_{10}O_3$; Glycerol -ether (Beilstein I. 314).-



This is prepared by distilling glycerol with $CaCl_2$ or better NH_4Cl. It is a liquid of boiling point 171°-172°; miscible in all proportions with water, specific gravity 1.145 at 0°, 1.16 at 15° and 1.097 at 18°. It combines with water at 100° to form acrolein.

Nef attributes its formation to the dissociation of the chloride, giving hydrochloric acid. α and β chlorhydrins are formed. These decompose at 440° into the isomeres α and β - dioxypropylidenes which then form acetol and hydracrylic aldehyde as glycerol does on dehydration. Acrolein is then formed which unites to form α acrolein-glycerol. In the presence of hydrochloric acid intramolecular addition takes place forming β acrolein-glycerol.



$$OH_2{=}CH{-}CH\begin{matrix}\diagup O{-}CH_2\\ \;|\\ \diagdown O{-}CH{-}CH_2{-}O{-}H\end{matrix} \rightarrow \underset{O}{CH_2}{-}CH_2{-}CH\begin{matrix}\diagup O{-}CH_2\\ \leftarrow O{-}CH_2\\ CH_2\end{matrix}$$

This may only be expected in the presence of chloride. The presence of chlorides should be avoided/since besides their formation of acrolein glycerol, they aid the formation of acetol and formaldehyde-glycerol.

<u>Crotonaldehyde</u>.- This was found in traces by Nef (Ann. <u>335</u>, 222). It comes no doubt from condensation of the acetaldehyde.

<u>Gas</u>.- Nef (Ann. <u>335</u>, 210) obtained 1.9 liters of gas in the distillation of 250 g. of glycerol; its analysis by absorption gave CO 80.3 cc., H_2 12.4 cc. When acrolein

polymerises in ultraviolet light, it gives a gas analysing $CO = 80\%$, $H_2 - 5\%$, $CO_2 = 5\%$, and C_2H_2 and hydrocarbons = 10% (Berthelot and Gadechan (Compt. rend. 151, 1349). Lockeman u. Liesche (J. Prakt. Chem. 71, 493) found $O_2 = 1.9\%$, $H_2 = 17.1\%$, $CO = 63.0\%$, $CH_4 = 18\%$, and traces of ethylene and propylene. $(CH_2O \rightleftarrows CO + H_2)$.

Acrylic Acid.- Oxidation of acrolein in the air gives acrylic acid.

Propylene.- This was observed by Westphal (Ber. 18, 2931) in the use of zinc dust as a catalyzer but was not verified by Nef (Ann. 335, 219) after a careful research.

Phenol.- Phenol is found in the higher boiling residue from which it may be freed by adding alkali. It is believed to come from glycerol ether. (Linnemann and Zotta (Ann. Suppl. 8, 254) $C_6H_{10}O_3 = C_6H_6O + 2\ H_2O$.

Allyl Alcohol.- This was found in the distillation from zinc dust by Westphal (Ber. 18, 2931) and in the distillation from calcium chloride by Linnemann and Zotta (Ann. Suppl. 8, 254).

Acetone- Propionaldehyde.- These were found in the distillation from calcium chloride by Linnemann and Zotta (Ann. Suppl. 8, 254).

TRIMETHYLENE GLYCOL

The preparation of acrolein from trimethylene glycol was suggested by the facts that: (1) Al_2O_3, ThO_2 and other oxides split off H_2O from ethyl alcohol yielding ethylene and water:

$$H_3CCH_2OH \longrightarrow CH_2 = CH_2 + H_2O$$

(2) Reduced metals, such as Ni and Cu will, on the other hand, split off hydrogen and give acetaldehyde--

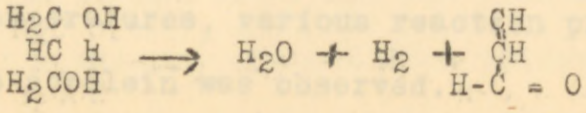
$$CH_3CH_2OH \longrightarrow H_2 + CH_3CHO$$

(3) Certain metallic oxides exert a mixed catalytic function on alcohols, the reaction velocity of the two reactions depending on the catalyst used. ZrO_2 and TiO_2 catalyze the two reactions to about the same extent (J. Phys. Chem. 1917, 21, 676).

This suggested trying to split off both water and hydrogen from trimethylene glycol.

It was found that trimethylene glycol is catalytically decomposed by a mixture of Al_2O_3 and copper at a temperature of 300-400° yielding acrolein in fair quantities, considering that the recovery of undecomposed glycol is good. Engelder (B.M. IX-21) believes that a 50% yield might be obtained. Copper alone also will decompose the glycol, giving acrolein, but Al_2O_3 does not. $MgSO_4$ decomposes trimethylene glycol but no acrolein is formed.

The mechanism of this reaction may be assumed to take place as follows:



$$\begin{array}{l} H_2C\ OH \\ HC\ H \\ H_2COH \end{array} \longrightarrow H_2O + H_2 + \begin{array}{l} CH \\ \| \\ CH \\ | \\ H\text{-}C = O \end{array}$$

The action of the copper might be explained by assuming that it first splits off hydrogen and that the unstable residue then loses water.

This method gives a smaller yield of byproducts than is obtained with glycerol.

Propylene glycol, $HOCH_2$ CHOH CH_3 , was treated similarly and while complete decomposition takes place with the formation of much gas, no acrolein is formed.

Normal propyl alcohol, $CH_3CH_2CH_2OH$, when passed over nickel, gave no results (B.M. XII-32).

ETHYLENE AND CARBON MONOXIDE.

Evans (B.M. VIII-8) has made a thorough study (cf. also Engelder, B. M. XII-32) of the interaction of ethylene and carbon monoxide, hoping to obtain acrolein:

$$CH_2{:}\ CH_2 + CO = CH_2{:}CHCHO$$

The catalysts studied were: finely divided nickel, platinized asbestos, heated charcoal (production of nascent CO from CO_2) and copper gauze. No acrolein was formed.

ACETYLENE, HYDROGEN, AND CARBON MONOXIDE

When these three gases were passed over contact copper (J. Am. Chem. Soc., Sept. 1917) cuprous chloride or charcoal at various temperatures, various reaction products were formed but no acrolein was observed.

ACETYLENE AND METHYL ALCOHOL

Acetylene and methyl alcohol vapor were then passed over copper gauze at temperatures up to 350° (with the idea that the methyl alcohol would be decomposed into hydrogen and carbon monoxide, which would then react with the acetylene to form acrolein) but no trace of acrolein was found.

ACETYLENE AND FORMALDEHYDE

Acetylene and formaldehyde were also studied but no acrolein was formed when these substances were passed over nickel, platinized asbestos or into cupric chloride solution containing copper.

Acrolein is prepared by the Societe des Matieres Colorantes, Usines Poirier, Rue des Poissoniers, St. Denis Seine, as follows:

Glycerine is dehydrated by heating in a cast iron retort with constant mechanical agitation with potassium bisulphate and with potassium sulphate as a catalyst. 40 kgs. of potassium sulphate are used with 200 kgs. of bisulphate. This mixture will dehydrate 2000 kgs. of pure glycerine or 1200 to 1500 kgs. of impure glycerine. After each charge of glycerine the bisulphate in the retor is dissolved in hot water and run into a decanter. After 12 hours the clear upper solution is drawn off and concentrated by heating. The bisulphate which crystallizes out may be used for another charge of glycerine.

The success of this reaction depends upon a constant temperature and a very slow dripping in of the glycerine with constant agitation.

The impure acrolein vapors pass into a copper chamber cooled with running water. These partially condensed vapors pass into the bottom of a cast iron tower filled with perforated shelves, upon which much of the water vapor is condensed. This tower is carefully heated with steam so that the temperature of the vapor is always 70°. These vapors (heated to 70°) are condensed in a cast iron decanter with cold water. It is necessary to remove all the water mixed with the acrolein, for there are present traces of many organic acids which are soluble in water. Acidic acrolein resinifies very readily, hence the necessity of removing the water solution of these acids.

The water which separates in this first decanter is drawn off at the bottom and piped back into the distilling tower. The upper layer of liquid acrolein passes by a constant level escape pipe into a 2nd cast iron decanter, from the bottom of which the last traces of water are also piped back to the distilling tower as they separate. It is now necessary to neutralize the last traces of acidic impurities in the acrolein to effectively prevent resinification. But just as acidic acrolein readily polymerises so does also alkaline acrolein. It is therefore necessary to use a weak alkali such as sodium bicarbonate.

This acrolein may be shipped in cast iron drums.

PROPERTIES.

A liquid with pungent smell. B.P. 52.4°. Oxidizes easily in the air to acrylic acid.

It is soluble in 2-3 parts of water, HNO_3 (1.2) oxidizes it to a mixture of glycollic and oxalic acids; chromic acid to CO_2 and HCOOH (Claus , Ann. Suppl. 2, 118). Zinc and HCl reduces it to allyl alcohol and acropinacone ($C_6H_{10}O_2$).

The specific gravity is 0.84 (H_2O = 1).

The polymerization of acrolein is described below:

POLYMERIZATION

POLYMERIZATION INTO DISCARYL

When acrolein is purified carefully, a perfectly clear liquid is obtained. But at the end of a variable and relatively short time, turbidity is seen to appear, then a white precipitate. Redtenbacher (Ann. 47, 141(1883), the first author to observe it, gave to this precipitate the name of "disacryl". Gradually the precipitate becomes more abundant and more compact and encroaches upon the whole mass of liquid. The phenomenon continues in this way until the acrolein has completely disappeared. It is a curious fact, that, although the formation of the discaryl takes place with contraction, all the glass receptacles, in which the observations are made, are found to be broken sooner or later, whatever be their thickness, as if the phenomenon involved an expansion or swelling. It is observed, in addition, that the pieces of the broken vessel continue to break into still smaller fragments as long as the disacryl which adheres to them is impregnated with acrolein. This shows that the formation of disacryl develops considerable local pressures on the walls of the vessels.

Properties of Disacryl.- At the beginning of the polymerization this product appears sometimes in the form of light flasks and sometimes in the form of a dense, extremely fine powder, which gathers at the bottom of the vessels, and assumes, under the microscope, the appearance of a mass of small transparent spheres.

Toward the end of the polymerization, it consists of light masses, having at times a fibrous texture, soft to the touch and readily pulverized between the fingers. This substance hardens in time and becomes brittle. Sometimes it is obtained, also, in lustrous, hard, elastic, concretions, whose appearance recalls that of ivory; this last appearance is always observed in those parts which are in contact with the glass surface, but which possess very slight thickness.

Disacryl is an inactive substance, odorless and tasteless, and appears insoluble in all neutral solvents. When first formed it is slightly soluble in concentrated nitric acid; an excess of water added to the liquid, precipitates a white product which we have not yet studied. Disacryl is infusible and does not distil.

Chromic acid mixture, fuming nitric acid, and the caustic alkalis attack it only very slowly. The determination of disacryl presents no difficulty; it is collected on the tared filter, washed with alcohol and dried to constant weight.

Cause .- The polymerization into discryl seems to be due to a spontaneous modification of acrolein and not to the action of foreign substances or impurities. A sample of acrolein was purified as follows:

A volume of about 6 litres was subjected to a series of three purifications in an apparatus provided with a Vigreux column, 50 cm. long. Such purification was preceded by a washing with a solution of sodium bicarbonate, followed by a drying over calcium chloride. The distillation was carried on very slowly and each time the first and last fourth was reheated; only the main portion, therefore, was subjected to further treatment. During each of these distillations the thermometer did not vary by more than a half figure. Finally in this way about half a litre of very pure acrolein was obtained.

Such a specimen remained clear during a period not exceeding twelve hours; then it began to become turbid in consequence of the formation of disacryl.

The action of the glass on acrolein tends to oppose the formation of disacryl. Acrolein kept in metallic containers changes into disacryl just as it does in the glass. The action of the air upon acrolein clearly promotes the formation of disacryl but air is not necessary to cause the phenomenon of polymerization into disacryl.

The degree of purity possessed by acrolein is of great importance as far as it concerns the speed of polymerization into disacryl. When acrolein is very pure, its polymerization is slow. However, it is known, that crude, that is to say, impure acrolein, such as the industry produces under the name of papite, is kept without perceptible change in darkness in metallic containers. In the course of its preparation, a mixture of water vapor is condensed, passing over at a temperature of 75°-80° instead of 52° (boiling point); a certain quantity of water is thus distilled, the excess of which is then separated by decantation, and in short, not only are the products carried by the acrolein vapor collected, but also the products carried by the water vapor. Since acrolein distilled after drying is unstable, it must be concluded that the stabilizing products of acrolein are capable of being carried by the water vapor but not by the dry acrolein vapor. We may add, that in order to obtain a stable product, it is not sufficient to distil the acrolein without previous drying; it is necessary to distil simultaneously a quantity of water such that the mixture of the vapors passes over at a temperature of 75°-80°.

It can be seen then from the practical point of view, how important it is, in order to obtain a stable acrolein, not to depart from the technical scheme of operations during the initial study of this product.

The action of heat is the clearest; it accelerates the formation of disacryl.

The accelerative influence of light upon the formation of disacryl has been seen by the accumulation of the first flakes in the part of the flasks exposed to the strongest light.

POLYMERIZATION INTO GUM.

When acrolein undergoes the change which we designate under the name of "gum polymerization", no change is observed at first in the appearance of the liquid in process of transformation. This kind of change is easily revealed by measuring the density, which is found to increase steadily and by the determination of the properties of the residue which the product leaves behind on evaporation. But when the proportion of gum reached 15%, the liquid loses its fluidity and becomes more and more syrupy in the proportion as the transformation progresses. It passes through all the stages of viscosity, ending, finally in a hard, brittle, transparent mass, which keeps for a long time the characteristic odor of acrolein.

The two processes of polymerization (disacryl and gum) do not appear capable of being produced simultaneously in the same liquid. We have already observed that acrolein is transformed either into disacryl or gum, but the two transformations never seem to occur at the same time. However, the change can begin in one direction and then proceed in the other. An initial polymerization into disacryl is frequently observed, soon giving place to polymerization into gum in such a way that the mass is at the same time rendered viscous by the gum and opaque by the flakes of disacryl.

The substance which we designate under the name of "acrolein gum" is a product very soluble in acrolein, acetone and alcohol, slightly soluble in various organic solvents (benzene, ether), very slightly soluble in water.

The gum has the property of holding acrolein strongly and consequently of diminishing the vapor pressure of that liquid. When a specimen of acrolein partially polymerized into gum is distilled, it is found that it is necessary to raise the temperature of the warming bath progressively, in proportion as the gum is concentrated; the viscous residue still retains at 100° a perceptible quantity of acrolein, and it is not eliminated entirely even when the heating takes place under a very slight vacuum. The formation of this material is, therefore, from the point of view of military use, more detrimental than that of disacryl, since the loss of activity by the initial product is, in this case, greater than that corresponding to the weight of the polymeri substance formed .

Since the gas is not a definite product, an accurate determination cannot be obtained. Moureu considers as "gum" the residue which a changed acrolein leaves in distillation when the latter is conducted with the precautions we shall indicate.

The formation of the gum takes place with contraction. It is always possible by measuring the density to show very directly when the change begins and to follow accurately its whole progress. Polymerization into gum has been observed only in impure forms of acrolein. If various pure substances are added to acrolein, it is found that free bases or salts or else substances capable of becoming basic alone cause the formation of the gum. Furthermore,in cases in which polymerization into gum took place, Moureu has been able to reveal or at least to suspect the presence of basic impurities and especially of metallic salts.

Acrolein can remain unchanged for a long time with a very pronounced acid reaction, but it does not resist for more than a few minutes the action of free alkalies, even when the latter are used in proportions hardly sufficient to cause reddening of the liquid in presence of phenolphthalein.

It is very generally to the action of metallic salts that must be attributed polymerizations into gum observed in actual practice. Anhydric iron perchloride and cupric chloride, used in the proportion of 1/500, cause the total transformation in mass of acrolein in a period of time not exceeding three months.

Speed of the Phenomenon.- This speed depends upon the activity and concentration of the polymerization reagents; it is possible to obtain every degree of speed by varying these two factors. At a concentration of 1% ammonia gives a reaction of explosives rapidly. Brucine polymerizes suddenly with projections after a few minutes of contact, quinine polymerizes in a few hours, morphine in a few weeks, pyridine in a few months.

By using sufficiently weak concentrations of the most energetic reagents, their action can be regulated at will.

Heat seems to promote the formation of the gum as it does that of disacryl.

STABILIZATION

Amyl nitrite.- Early reports by the French seemed to indicate that 5% amyl nitrite stabilized acrolein. Later observations (Z-124) showed that while it did prevent the formation of disacryl, it seemed to promote polymerization into gum.

Copper.- Kohler (B.M.I,45) reports that the stabilization of acrolein is a simple matter and consists simply in the addition of a small amount of metallic copper. This keeps acrolein in the liquid condition indefinitely whether the sample be pure or impure. Even if the polymerization has started, it is immediately arrested by the addition of copper. Tubes containing acrolein with copper have been heated for a period of 24 hours at 300° without showing any change.

Moureu finds that copper also prevents the formation of disacryl but it promotes the polymerization into gum. The stabilizing action of copper is due to superficially oxidized copper and not with carefully sconned copper.

Perrott, Yablick and Feld (B.M. XII-II) reached a similar conclusion. From the behavior of copper it was thought that copper acted as a deoxidizer. The copper tarnished, forming an oxide of copper, which later dissolved (green color of the acrolein). If the cuprous salt acted as a stabilizer, it seemed simpler to add a solution of a salt. 10 drops of a saturated alcoholic solution of cuprous chloride, added to 50 cc. of acrolein, preserved it unchanged for 20 days.

Perrott and Yablick (B.M. XIX-21) continued these experiments for a period of 4 months and confirmed the earlier result. 0.5 gm. cuprous chloride per liter will effectively stabilize acrolein even in the sunlight.

Other experiments indicate that Na_2SO_3 , traces of $SnCl_2$ (0.022 gm. per 50 cc.) or Iodine 0.4 gr. per liter are also effective in the preservation of acrolein when kept in the dark. Phosphorus and aluminium amalgam were also more or less effective.

The behavior of the different agents is seen in the following table:

SERIES A.

RESULTS:

Glass stoppered bottles containing 50 c.c. acrolein kept in dim diffused light.

STABILIZING AGENT	ELAPSED TIME TO VISIBLE CHANGE.	APPEARANCE AFTER 30 DAYS.	APPEARANCE AFTER 120 DAYS.
1. Aluminum amalgam	2 days		About 40% converted to a white gelatinous mass.
2. Yellow phosphorus	2 days		About 20% converted to white solid.
3. Crystals Na_2SO_3 in alcohol		Clear and liquid.	Sticky viscous mass.
4. 0.02 g. $SnCl_2$ per 50 c.c.	Yellow tinge in 1 day.	Yellow liquid.	Viscous as lubricating oil.
5. 0.04 g. $SnCl_2$ per 50 c.c	Yellow tinge in 8 hours.	Somewhat viscous.	Solid glue-like mass.
6. 0.05 g. $SnCl_2$ per 50 c.c.	Yellow tinge in 8 hours.	More viscous than #5.	Solid glue-like mass.
7. 0.06 g. $SnCl_2$ per 50 c.c.	"	Consistency of lubricating oil.	"
8. Copper shot	21 days.	Solution green and gelatinous deposit formed.	Gelatinous deposit increased; some solid formed.
9. Nothing added.	1 hour.	Dense white solid.	
10. Cuprous chloride 0.02 g. per 50 c.c.		Slight amount sediment formed when first added; no visible change with time.	No apparent change

SERIES B.

Glass stoppered bottles containing 50 c.c. acrolein kept in direct sunlight:

MATERIAL ADDED	ELAPSED TIME TO VISIBLE CHANGE	APPEARANCE AFTER 30 DAYS.	APPEARANCE AFTER 120 DAYS.
Cuprous chloride		No apparent change.	No apparent change.
Copper shot	1 day.	Dense greenish solid in 1 day.	
Stannous chloride	1 day.	Opaque viscous mass in 3 days.	
Iodine	3 days.	Iodine color bleaches; viscous mass formed.	
Yellow phosphorus	1 day.	Dense white solid in 3 days.	

An extensive study of the stabilization of acrolein has been made by Moureu (Z-124). Without discussing in detail the mass of experimental data there reported, it may be said that he has found very satisfactory stabilizing agents in the polyhydrin phenols: 1-1000 of pyrogallol, 1-500 of pyrocatechol or hydroquinone, 1-250 of gallin acid or 1% of tannin extract of gall nuts. From the amount of acrolein changed in one day, he calculates the life of specimens of acrolein stabilized as above to be from 14 to 27 years. The calculation, although it has no objective value, is given in order to show more strikingly the slowness of the change.

ANALYSIS

QUALITATIVE.

Teague and Yoe (B.M. IX-15) have used a very dilute (0.0004N) potassium permanganate solution which has been acidulated with sulfuric acid, (1.26 gm. $KMnO_4$ are dissolved in 1 liter water. 10 cc. of this solution are then diluted to a liter and acidified with a little dilute sulfuric acid). The decolorization of this solution indicates the "break" of the canister.

Hill (B.M. III-21) found that 0.000316 gm. $KMnO_4$ (25 cc. of a 0.01 N solution containing 2 cc. concentrated H_2SO_4) was decolorized in one second. Passage of laboratory air for 20 minutes caused no color change.

It is possible to detect the odor of acrolein 2 or 3 minutes before the potassium permanganate solution is decolorized.

Magenta solution (0.1 gm. per 1000 cc. water) changed in 2-3 minutes.

Hill further tested a solution made by adding 0.5 gm. sodium nitroprusside, in water solution, to 15 cc.

piperidine and diluting to 100 cc. Using a constant small supply of acrolein vapor this solution underwent a color change in 50 seconds, becoming green by transmitted light, and violet red by reflected light. If diluted further, the reagent becomes erratic and inefficient as an indicator.

Tsalapotanis (Anales soc. quim. Argentina, 5, 244(1917) has used Cramer's reagent for detecting acrolein in the following manner: 1-2cc. of an aqueous solution of resorcinol and several drops of a 10% NaOH solution are added to the liquid to be tested and the mixture is heated; after about 2 minutes a bluish green color in the case of dilute solutions and a red color in the case of concentrated solutions is obtained. The color disappears when acids are added and reappears after addition of alkali; the color is quite stable in alkaline solutions.

QUANTITATIVE

Yoe (B.M.VII-14) devised the following method of analysis in connection with the testing of efficiency of canisters:

A measured volume of air containing the acrolein vapor was passed through an electric furnace heated to 800° or 900°C. The carbon dioxide thus formed passed from the furnace into barium hydroxide solution contained in small glass cylinders. A large excess of barium hydroxide solution was used, the excess being determined by titration with oxalic acid, using phenolphthalein as an indicator. By difference, the amount of barium hydroxide that combined with the carbon dioxide was obtained and from this was calculated the amount of acrolein present. From the pressure line the air was forced first through a 40% potassium hydroxide solution to remove the carbon dioxide of the air and then through concentrated sulphuric acid to remove any potassium hydroxide. The air was passed on through the flask and the 3/4" silica tube of the furnace, filled with small pieces of unglazed porcelain. At the other end of the furnace tube were several glass absorbent cylinders, each containing 50 cc. of 0.02 N barium hydroxide solution. A wet meter was connected to the last cylinder of the series, the meter being attached to the suction line.

The furnace having been heated to 800° or 900°C., air was forced through the apparatus for 10 or 15 minutes or until a two-liter sample showed the absence of carbon dioxide. The bulb containing acrolein was then broken, the pressure and suction turned on and the gaseous mixture drawn slowly through the furnace. 1/3 liter per minute. Five liter samples were taken till, by analysis, the apparatus was shown to be carbon dioxide free.

Immediately upon starting the sampling a low Bunsen flame was placed under the beaker of water containing the flask in which the bulb of acrolein was broken. By the time the apparatus was shown to be carbon dioxide free, the water in the beaker was boiling, thus insuring the complete vaporization of any acrolein which might have been in the capillary end of the bulb, the boiling point of the water being considerably above that of the acrolein.

The maximum deviation from the mean value of the acrolein was 5%. This is probably no greater than one should expect when the large volumes of barium hydroxide solution and the small amounts of acrolein are considered. (.0066 to .0137 gm. of acrolein were used in the above analyses).

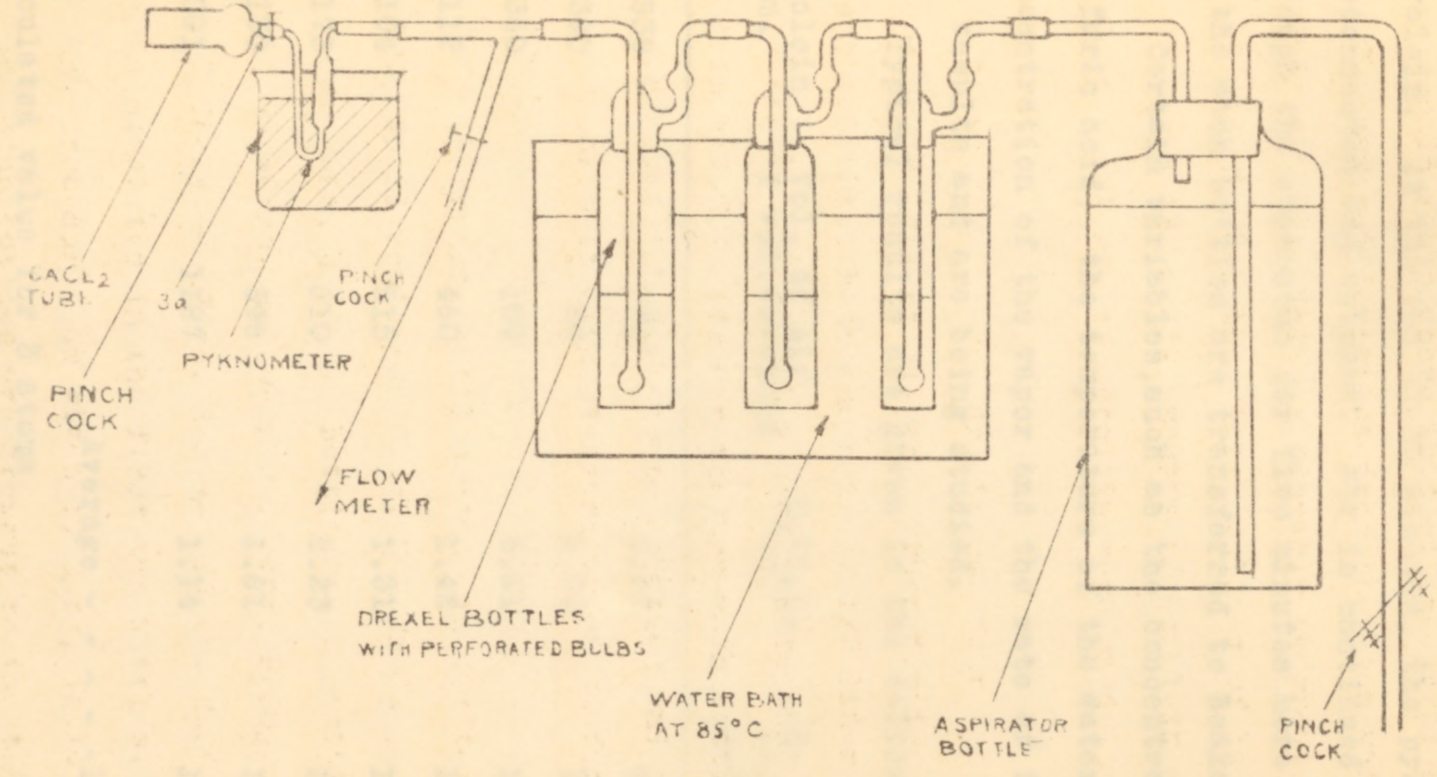
It was found necessary to use four cylinders of baryta in series to collect all the carbon dioxide when the latter is bubbled through at the rate of 1/3 liter per minute.

Mark (B.M. IX-22) has proposed to pass the vapor of acrolein diluted with air through wash bottles containing standard potassium dichromate solution and to titrate the excess dichromate with standard ammonium ferrous sulfate (Plate II).

The absorption bottles stand in a water bath at 83-87°. No. 1 contains 20 cc. N $K_2Cr_2O_7$, 80 cc. H_2O , and 2 cc. conc. H_2SO_4 . Bottle No. 2 contains 10 cc. $K_2Cr_2O_7$ + 90 cc. H_2O + 2 cc. conc. H_2SO_4 . No. 3 contains 3 cc. $K_2Cr_2O_7$ + 27 cc. H_2O + 0.6 cc. H_2SO_4. The absorption is completed in the first two bottles.

The procedure, as given by Mark, follows:

The wash bottles are brought to the temperature of the bath. The weighed pyknometer and contents are attached.



APPARATUS USED IN ANALYSIS OF
ACROLEIN
PLATE II

A steady flow of air at the desired rate is obtained and then, by opening a pinch cock on the pyknometer, a very slow stream of bubbles of air is passed through the acrolein. At the end of 30 minutes, the pyknometer is disconnected and weighed. Air is continued to be drawn through the apparatus for five minutes more and the contents of the wash bottles are transferred to beakers and titrated.

Certain variables, such as the concentration of sulfuric acid, the temperature of the water bath, the concentration of the vapor and the rate of flow, affect the results and are being studied.

Typical results are given in the following table:

Acrolein gm.	Vol. of Air 1 vol. acrolein	$K_2Cr_2O_7$ cc.	N. $K_2Cr_2O_7$ cc. - 1 gm. acrolein
0.0538	70	6.97	106
0.0390	84	6.02	100
0.0360	109	4.61	104
0.0112	460	1.42	104
0.0104	515	1.31	103
0.0173	610	2.23	105
0.0130	896	1.61	101
0.0091	1187	1.14	103

Average - - - - -103.2

Calculated value for 3 atoms of oxygen to 1 molecule acrolein 102.3

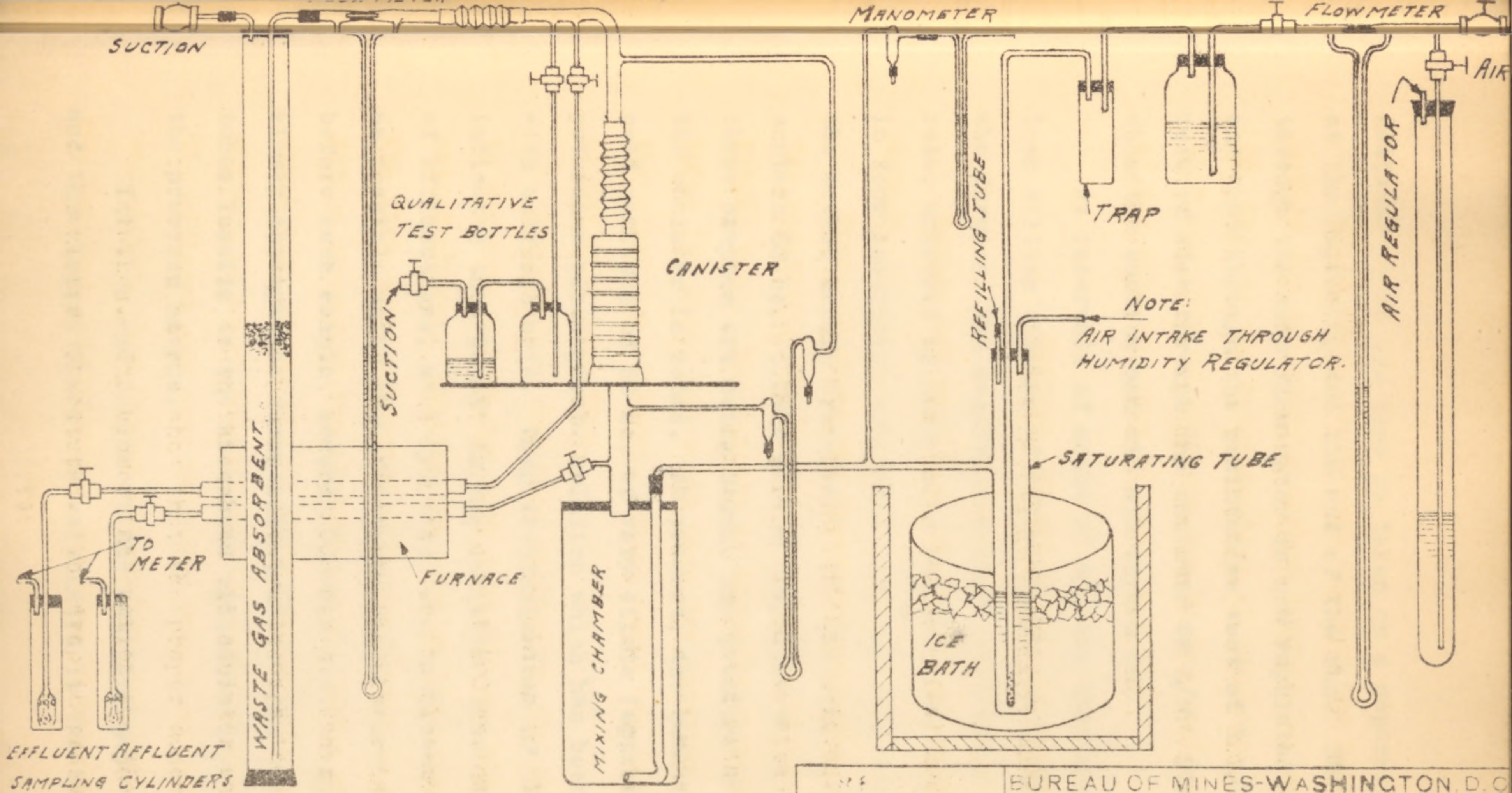
Coith (B.M. II-10) has applied the Higgins-Marriott method for determining carbon dioxide (J. Am. Chem. Soc. 39, 68) to the determination of acrolein. He finds that one part of acrolein can be detected in 15,000 parts of air with an error of less than 12%.

TESTING THE EFFICIENCY OF CANISTERS.

Teague and Yoe (B.M. IX-15; XXI-4) used the following method.

Plate III shows the apparatus employed. A humidifier for regulating the humidity at 50% is attached to the air intake tube. The furnace is supplied with two quartz tubes (¼" bore) one being used for entering samples and the other for effluent. These tubes are filled with pieces of unglazed porcelain.

Procedure.- The tube containing the liquid is filled to the same height for each test (20 cm. has been found satisfactory). Holding the suction flow-meter at 32 L/M, the flow-meter connected with the blower is adjusted to give a concentration of 5000 p.p.m. Under present conditions about 1/10 of the air is blown through the liquid. The mixture is drawn through an old canister until tests of the effluent gas show that the proper concentration is being maintained. The blower and suction are then closed and the new canister substituted. The drop in pressure across the



BUREAU OF MINES-WASHINGTON, D.C.
GAS INVESTIGATIONS

SCALE: ——
DRAWN BY C.W.L.
TRACED BY C.W.L.
CHECKED BY J.H.Y.
DATE 12-8-17

APPARATUS FOR
TESTING THE EFFECTS OF
CANISTERS AGAINST ACROLIN

PLATE III

canister at 85 L/M flow is taken on a separate apparatus at the beginning and the end of the run. The suction through the main flow-meter is now regulated to 31 L/M and that through the qualitative test at 1 L/M, making the rate of flow through the canister 32 L/M. Time is taken when the suction and air are turned on.

At intervals of about 20 minutes throughout the "run", 1-or 2-liter samples of effluent gas are withdrawn through the furnace. The samples are taken at $\frac{1}{4}$ liter per minute rate, measured by means of a standard wet meter, absorbed in four absorption cylinders, and analyzed according to the method herein described. The absorption cylinders each contain 50 cc. 0.03 N barium hydroxide solution. While these samples are being taken, the pressure drop through the canister is noted. At present, the qualitative test used consists of 50 cc. of very dilute (approx. 0.004 N) potassium permanganate solution which has been acidulated with sulfuric acid. When decolorization of this solution indicates the "break" in the canister, five-liter samples of effluent gas, at $\frac{1}{4}$ L/M rate, are withdrawn as frqquently as possible until the efficiency falls below 80%. Just before each sample, several hundred c.c. of gas are drawn slowly through the furnace. ($\frac{1}{4}$ L/M) in order to sweep the tubes leading to the absorbent cylinders free of gas of the previous sample.

The time and length of the sampling periods are noted and the elapsed times are calculated in the middle of these periods. The efficiency is calculated on the basis of the nearest effluent concentration. The observed pressure drops must be corrected for the drop through an empty canister. The humidity and average temperature during the test are recorded.

Note.- The efficiency of the qualitative test has been found to be about 100%. As a check, however, a small bottle (which is kept in series) of the effluent gas is removed just after the decolorization of the permanganate solution. A very faint odor of gas is obtained. (If the test lasts for more than 2 hours. a fresh qualitative test solution should be inserted.) It is possible to detect the odor of acrolein 2 or 3 minutes before the potassium permanganate solution is decolorized. The odor test will be considered the 100% efficiency point.

Analysis.- The gas samples pass through the furnace which is heated to about 900°C. The acrolein is burned and the carbon dioxide thus formed is absorbed in 0.03 N barium hydroxide solution. The excess barium hydroxide is determined by titration with 0.03 N oxalic acid, using phenolphthalein as an indicator. A blank is used for the carbon dioxide in the air. This is subtracted from each liter. For a one-liter sample this correction is about 1 c.c. barium hydroxide solution. The acrolein is calculated as parts per million at 25°C and 760 mm. pressure.

Calculations.- In a one-liter sample, a c.c. of 0.03 N $Ba(OH)_2$ solution = 122.25 p.p.m. gas at 25°C and 760 mm. pressure. 5000 p.p.m. = 11.46 mg. per liter.

ABSORPTION

Hill tested charcoal against 0.08% acrolein, with a rate of flow of 540 cc. per cm^2 per minute and found the following values:

34 min.	100% efficiency
60 "	98% "
86 "	87 "
105 "	77 "

Fuller's earth gave qualitative tests from the start and after 10 minutes showed 38% efficiency.

Permutite and sawdust did not absorb at all.

PROTECTION

M-5 states that acrolein goes through the German mask and through the old French mask.

The French propose the following protection: Pumice incorporated with 9% of its weight of crystallised chromic acid (not solution). Deliquesence of the acid causes impregnation of the pumice.

Teague (B.M.IX-14) reports that the canisters tested (Bec. 10, 1917) furnished good protection against acrolein. In B.M.X-23, the U.S.Canister in use at that time is reported as furnishing protection against 5000 p.p.m. for 53 minutes as compared with 28 minutes for HCN and 28 minutes for 4000 p.p.m. of chlorpicrin.

Permeability tests by Perrott and Feld are given in B.M.IX-8. A Goodrich rubber sheeting MR#6 , held for 60 minutes (the same fabric held for 500 minutes against chlorpicrin.)

PHYSIOLOGY

Acrolein is a lachrymator and respiratory irritant; the effects on the eyes and throat occur simultaneously. In concentrations of 0.025 mg. per l. it develops an irritating action, secretions of saliva, weeping from the eyes, nose secretions and slight narcosis. Frankel says that acrolein is highly irritating and but little antiseptic.

Action on Man.- One part in 200,000 acts as a lachrymator and nasal irritant, while 1 part in 100,000 is intolerable (Ph-31).

The minimum effective concentration (with or without eye protection) is 1 in 100,000 (0.025 mg. per 1). The toxicity is about the same as phosgene.

The gas causes nausea and heart trouble (depression and partial paralysis) and also affects the memory (M-5).

Action on Mice.- Kolls, Kuhn and Todd (B.M.III-48) using a sample of acrolein boiling at 52.6° and exposing the mice for 10 minutes, found the immediate toxic concentration to be between 0.55 and 0.38 mg. per liter (that which kills over 50% of the mice exposed for 10 minutes within 48 hours) The delayed toxic point (that which kills after 48 hours and in less than 10 days) is between 0.16 and 0.17 mg. per liter.

Symptoms.- In concentrations of 1 mgm. or more there was increased excitement, but lower concentrations produced depressions. All concentrations caused irritation as shown by rubbing of noses and closing of eyes. Gasping was also a constant symptom, it being only occasional with the low concentrations, but continual with the highest concentration, 4 mgm. The delayed deaths above took place in from 48 to 65 hours.

Concentrations of 4.1 mgms. killed all four mice within 7 min. in bottles. They showed violent excitement from outset and died with convulsions. Moderate concentrations killed all within from 1-46 hours.

Action on Rats.- One part in 1,000 killed in 50 minutes (Ph-3).

Action on Cat.- A dose above 0.04 mg. per l. causes such intense irritation that some days are required for recovery. With 0.2 mg. the lung irritation phenomena are not recognizable but are obviously painful and the muscles come into activity. A dose of 1.5 mg. seriously affects the animal, which dies 18 hours after a 2.25 hour exposure to the gas, of pulmonary edema and bleeding of the lungs; with a dose of 1.98 mg. death sets in 2.5 hours later. (Kober and Hanson, Diseases of Occupation, p.720).

Action on Dogs.- Miller (B.M.X-58) reports the following symptoms: During exposure-- The dogs are very excited during the early part of the exposure. The eyes and nose are immediately irritated and the animal blinks and licks his nose the instant the gas is turned on. Lachrymation and salivation are both profuse. After a short time the animals keep their eyes tightly closed. The cornea is usually dulled. Nasal secretion is very much increased. Respiration is early affected becoming very slow and labored. Towards the end of the exposure the animal is usually very depressed. Subsequent symptoms.-- Within a few hours after exposure the animal develops a severe tracheal rattle, is very depressed, coughs, and has very labored respiration. The eyes are sore and the cornea is usually dulled. With toxic concentrations death occurs in four hours to two days. With non-toxic concentrations the animal is very sick for several days and does not fully recover for a week or more.

The toxic concentration may be placed at 0.35 mg. per liter.

Ph-2 reports that 0.5 mg. per l. killed in 6 hours.

SENSITIVENESS OF INDIVIDUALS.

Experiments to determine the smallest concentration of acrolein that can be detected by the eyes, nose, throat or lower respiratory tract (Sherwood, Snyder and Gavin, B.M. XIII-59) show that acrolein is detectable by its odor at a concentration of 0.0028 mg. per liter or 1.12 p.p.m. and that some individuals will detect it at even smaller concentrations. When the amount of gas is increased to 0.0077 mg. per liter (3.06 p.p.m.) irritation of the eyes and nose become prominent symptoms in the majority of teste Lachrymation does not become prominent until the concentration reaches 0.010 mg. per liter or 4.00 p.p.m.

PATHOLOGY

Only two animals have been examined after exposure to this gas. There has been so much similarity in the lesions found, however, that a tentative description of the action of the gas will be given. The eyes are severel affected. At the end of two or three days a purulent conjunctivitis and heavy clouding of the corneal epitheliu have developed. As no animals surviving more than three days have been observed, the ultimate result of these lesions has not been determined. The mucosa of the mouth and nasal passages shows patches of reddening; and on the epiglottis and about the laryngeal orifice pin-head hemorrhages are found. The trachea and bronchi down to the smallest visible branches are lined by a semi-fluid purulent exudate of dirty yellowish-gray color. The enti bronchial tree is literally dripping with pus. The suppurative bronchitis is readily differentiated from the membranous bronchitis and trachitis of mustard gas dogs.

The former is frankly purulent, while the latter forms a distinct membrane which can be peeled off in sheets. The suppurative condition found in acrolein dogs is associated with an extreme congestion in the tracheal and bronchial walls. The lungs are composed of normal looking areas of pulmonary tissue mingled with patches of atelectasis, which are deep red, firm and airless. The collapse appears to be due to the plugging of bronchi with exudate. On section these lungs show numerous droplets of pus escaping from the openings of cut bronchi and also small patches of broncho-pneumonia.

Outside of these lesions of the eye and respiratory system, no noteworthy changes have been found.

TREATMENT

M-25 (Chemistry of Gas Warfare) suggests the following treatment: Immediate removal from the poisonous atmosphere; artificial respiration; inhalation of steam; faradic stimulation of the phrenic nerve; free blood letting; in case of obstinate spasm of the glottis tracheotomy.

TACTICAL USE

It has been shot in grenades and found effective. Use in shells would involve the use of a fumigen, which would interfere with the stabilization.

SHELL FILLING

Acrolein received in cast iron drums is a liquid under ordinary conditions and is fed without refrigeration by gravity to a chapel, in which a small feed pipe with a "constant empty space" manometer is used to fill grenades.

This filling is all hand work. The filler holds the grenade in his left hand and operates the feed valves with his right. When it is full he passes it to another operator who screws the gaine into the grenade with his right hand. A third man holds the grenade in his left hand and tightens the gaine with a wrench held in his right. All these operators wear heavy rubber gloves.

These grenades are quite fragile and must be handled and packed with care. Here no mellinite cartridge is used in the gaine the detonating charge of mercuric fulminate being sufficient to shelter the grenade.

This acrolein affects the eyes badly but its worst effect is the terribly oppressive suffocation that it produces when taken into the lungs.

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