30. *Promoters for the Dropwise Condensation of Steam. Part IV.* Discussion of Dropwise Condensation and Testing of Compounds.*

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The modes of condensation of steam on a cooled metal surface are discussed, and experiments are described to illustrate the relation between the activity and chemical constitution of compounds which promote dropwise condensation.

THE mode of condensation of water vapour on a cooled metal surface is important in connection with steam-condensation plants, where the aim is to transfer the heat from the steam to the cooling water as rapidly and as efficiently as possible. There are two clearly distinguishable ideal modes of condensation, namely, (1) filmwise, where the condensate forms a continuous film on the metal surface, and (2) dropwise, where the condensate forms small drops which are segments of spheres similar in shape but differing in size. The appearance of ideal dropwise condensation is shown in the Plate. In practical applications the condensed vapour is usually distributed over the cooled surface in an irregular manner. Some parts of the condensate approximate to drops, and others are areas of film thicker

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* Parts I—III, preceding papers.

than in the ideal case (1) defined above. This type of condensation is referred to as the "mixed" type.

There is considerable advantage in preserving purely dropwise condensation, particularly where large heat-transfer rates are desired, since the "surface" coefficient is of the order of 10 times, and the "overall" coefficient 2—3 times, that for condensation as a continuous film.

Several investigators [1] have examined dropwise condensation and established that in conditions of chemical cleanliness water condenses on a metal surface as a continuous film. In order that drops may form the interfacial tensions at the metal surface must be modified by the presence of a promoter. This, in general, will be a compound which consists of two main chemical parts, (*a*) a hydrophobic (water-repellent) group, and (*b*) a chemical group which has an affinity for the metal. Emmons [2] postulated that such a promoter was oriented at the cooled surface with the relatively active portion of the molecules attached in some way to the surface, while the inactive part was exposed to the vapour. This led to the conclusion that only one layer of promoter molecules on the surface could be responsible for dropwise condensation. (The same conclusion might be obtained from the work of Adam [3] and Rideal [4] who considered the surface orientation of fatty acids in connection with their limiting area of cross-section.) Emmons successfully tested his theory by depositing octadecanoic acid on initially clean surfaces: all the acid beyond one complete molecular layer was removed immediately by the condensing steam.

Dropwise condensation on steel and on copper-containing metal surfaces has previously been obtained by the use of fatty acids and certain other types of organic compound, but the duration of such condensation is far too short for industrial application. To maintain dropwise condensation for several thousands of hours it is necessary that the promoter should adhere strongly to, *i.e.*, be chemisorbed on, the surface.

The aim of the present work was to synthesise compounds which should be effective on copper and copper-containing metal surfaces. Sulphur and selenium have been incorporated in the surface-active groups because of their high affinity for copper. In most of the compounds (see Parts I—III [5]) the dodecyl and the octadecyl hydrocarbon chain were used as the water-repellent portion. It was hoped to correlate the structure of the compounds with the duration of the dropwise condensation that they produced. This, however, was not possible owing to the extremely long effects of all compounds tested. Nevertheless, valuable information was obtained on the relation between the promoter ability and structure. A description of an apparatus for testing the compounds, and the complete results of the tests obtained therein, will be published elsewhere.

RESULTS

It is suggested above that an efficient promoter must contain a surface-active group which adheres chemically to the metal surface. This was confirmed by the fact that $C_{12}H_{25}{\cdot}SO_3Na$ and $(C_{18}H_{37})_2SO_2$ were ineffective whereas $(C_{18}H_{37})_2SO$ was effective. In the first two compounds all the valency electrons of the sulphur are involved in chemical linkages, whereas in the last compound the sulphur atom has two valency electrons available for bond formation with copper. On this evidence only compounds which had sulphur or selenium in the bivalent state were synthesised.

Quality of the Condensate and Mode of Attachment of Promoter Molecules.—While it was obvious that certain compounds, *e.g.*, $C_{18}H_{37}{\cdot}SH$, would promote good-quality dropwise

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[1] Spoelstra, *Arch. Suikerind.*, 1931, **3**, 903; Schmidt, Schurigg, and Sellschop, *Tech. Mechanik u. Thermo-Dynamik*, 1930, **1**, 153; Old, *J. Inst. Mech. Eng.*, Dec. 1939, p. 199; Nagle and Drew, *Trans. Amer. Inst. Chem. Eng.*, 1933—34, **30**, 217; Jakob, *Mech. Eng.*, 1936, **58**, 738; Hampson and Özisik, *Proc. Inst. Mech. Eng.*, 1952, **1**, *B*, No. 7, 282.

[2] Emmons, *Trans. Amer. Inst. Chem. Eng.*, 1939, **35**, 109.

[3] Adam, "The Physics and Chemistry of Surfaces," Oxford Univ. Press, 3rd Edn.

[4] Rideal, "Surface Chemistry," Cambridge Univ. Press, 2nd. Edn.

[5] Blackman and Dewar, preceding papers.

condensation it was less obvious that other compounds would be equally effective. Visual observation showed that there was no difference in the quality of the drops promoted by

(C) 

$$C_{18}H_{37}\cdot O\cdot\underset{\underset{S}{\|}}{C}\cdot S\cdot[CH_2]_{10}\cdot\underset{\underset{O}{\|}}{C}\cdot S\cdot[CH_2]_{10}\cdot S\cdot\underset{\underset{O}{\|}}{C}\cdot[CH_2]_{10}\cdot S\cdot\underset{\underset{S}{\|}}{C}\cdot O\cdot C_{18}H_{37}$$

(D) 

$$HS\cdot[CH_2]_{10}\cdot\underset{\underset{O}{\|}}{C}\cdot S\cdot[CH_2]_{10}\cdot S\cdot\underset{\underset{O}{\|}}{C}\cdot[CH_2]_{10}\cdot SH$$

$C_{12}H_{25}\cdot SH$ (*A*) and $C_{18}H_{37}\cdot SH$ (*B*). This was expected since both compounds exposed the same surface ($CH_3\cdot CH_2\cdot CH_2$ . . .) for condensation. However, it was also found that compounds (*C*) and (*D*) promoted an apparently identical quality of condensation. In the latter compounds the molecules are almost certainly anchored to the metal surface at four positions, as represented in Fig. 1.

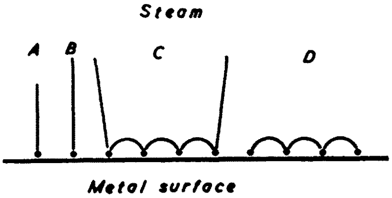


FIG. 1. *Suggested mode of orientation of molecules on a metal surface.*

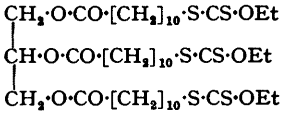
● *Sulphur atom bonding molecule to the metal surface.*
A, B, C, D, see text.

The compounds listed in Table 1 gave perfect dropwise condensation. They are representative of the complete range of compounds prepared in this work.

TABLE 1. *Compounds which promoted perfect dropwise condensation.*

(a) *Effective for at least 500 hr.* (*laboratory tests*).

$KS\cdot CS\cdot O\cdot[CH_2]_{10}\cdot O\cdot CS\cdot SK$
$EtS\cdot CS\cdot O\cdot[CH_2]_{10}\cdot O\cdot CS\cdot SEt$
$C_{12}H_{25}\cdot S\cdot CS\cdot S\cdot C_{12}H_{25}$
$C_{12}H_{25}\cdot S\cdot CO\cdot[CH_2]_8\cdot CO\cdot S\cdot C_{12}H_{25}$
$C_{12}H_{25}\cdot S\cdot CO\cdot[CH_2]_{10}\cdot SeCN$
$C_{18}H_{37}\cdot SCN$
$C_{18}H_{37}\cdot SeCN$
$NHAc\cdot CS\cdot S\cdot C_{18}H_{37}$
$C_{18}H_{37}\cdot S\cdot CO\cdot NH_2$
$C_{18}H_{37}\cdot SH$
$C_{12}H_{25}\cdot S\cdot[CH_2]_{10}\cdot S\cdot C_{12}H_{25}$
$(C_{12}H_{25}\cdot S)_4Si$
$(C_{12}H_{25}\cdot S)_3P$
$(C_{12}H_{25}\cdot S)_4P_2S_3$
$(C_{18}H_{37}\cdot O)PS\cdot SH$
$(C_{18}H_{37}\cdot O)_4P_2S_3$



$$\begin{array}{l}CH_2\cdot O\cdot CO\cdot[CH_2]_{10}\cdot S\cdot CS\cdot OEt\\ |\\ CH\cdot O\cdot CO\cdot[CH_2]_{10}\cdot S\cdot CS\cdot OEt\\ |\\ CH_2\cdot O\cdot CO\cdot[CH_2]_{10}\cdot S\cdot CS\cdot OEt\end{array}$$

(b) *Tested for only 2 hr.*

$C_{18}H_{37}\cdot O\cdot CS\cdot S\cdot[CH_2]_{10}\cdot CO_2H$ (*E*)
$C_{18}H_{37}\cdot S\cdot CS\cdot O\cdot[CH_2]_{10}\cdot O\cdot CS\cdot S\cdot C_{18}H_{37}$
$C_{17}H_{35}\cdot CO\cdot S\cdot C_{12}H_{25}$
$NHAc\cdot CS\cdot S\cdot[CH_2]_{10}\cdot CO\cdot S\cdot C_{12}H_{25}$
$HS\cdot[CH_2]_{10}\cdot CO\cdot S\cdot[CH_2]_{10}\cdot S\cdot CO\cdot[CH_2]_{10}\cdot SH$
$NHAc\cdot CS\cdot S\cdot[CH_2]_{10}\cdot CO\cdot S\cdot[CH_2]_{10}\cdot S\cdot CO\cdot[CH_2]_{10}\cdot S\cdot CS\cdot NHAc$
$NCSe\cdot[CH_2]_{10}\cdot SeCN$
$NH_2\cdot CO\cdot S\cdot[CH_2]_{10}\cdot S\cdot CO\cdot NH_2$
$C_{12}H_{25}\cdot SH$
$[C_{18}H_{37}\cdot S\cdot C(NH_2)]^+$ picrate$^-$
$C_{18}H_{37}\cdot S\cdot C_{12}H_{25}$

Poor-quality dropwise condensation, where the drops appeared to have a contact angle of only 60—90°, was obtained from $C_{12}H_{25}\cdot S\cdot[CH_2]_{10}\cdot CO_2H$ (*F*) and $C_6H_5\cdot S\cdot S(O_2)\cdot Me$ (obtained as a gift from Dr. R. D. Marshall), and pure filmwise condensation was obtained from $[(NH_2)_2CS\cdot[CH_2]_{10}\cdot CO_2H]^+$ picrate$^-$ and $HO_2C\cdot CH_2\cdot S\cdot[CH_2]_{10}\cdot CO_2H$.

The compounds giving pure dropwise condensation have a common feature, namely, they all possess an "unhindered" hydrocarbon chain of sufficient length to afford completely water-repellency. When the promoter molecules are attached to the metal surface by means of the sulphur atom(s) the hydrocarbon residue is exposed to the steam, which then condenses in drops. Thus, even $[C_{18}H_{37}\cdot S\cdot C(NH_2)_2]^+$ picrate$^-$, which may appear at a first glance to be polar (m. p. 125°), promotes perfect dropwise condensation. The situation is represented in Fig. 2. It is perhaps surprising that the glycerol trixanthate promoted dropwise condensation since one might expect the terminal grouping ($CH_2\cdot O\cdot CO\cdot$) to exhibit a polar effect: the linking of the α-carbon atoms probably causes a very low polarity, and hence the dropwise condensation.

The two compounds which promoted poor-quality dropwise condensation consist of two parts of approximately equal " length," one polar and the other non-polar. Thus the exposed surface is in a condition intermediate between the extremes for pure dropwise and pure filmwise condensation. The two compounds which promoted pure filmwise condensation expose only polar groups to the steam, which therefore condenses as a film.

The general situation is represented in Fig. 3 where compounds representative of the three types of condensation are illustrated. [Compound (*G*), $C_2H_5O{\cdot}CS{\cdot}S{\cdot}[CH_2]_{10}{\cdot}CO_2H$, did not give absolutely pure filmwise condensation, but the divergence was too slight to be listed as a form of mixed condensation. The condensate consisted of large flat irregular patches, probably owing to a trace of impurity in the promoter.] The successive shortening of the hydrocarbon chain from $C_{18}H_{37}$ through $C_{12}H_{25}$ to C_2H_5, while the polar chain remains constant ($\cdot[CH_2]_{10}{\cdot}CO_2H$), is responsible in this series for the increase in polarity of the resultant exposed surface and the corresponding change from dropwise condensation, through the mixed form, to filmwise.

FIG. 2. *Orientation suggested for amidinothio-octadecane picrate at the metal surface.*

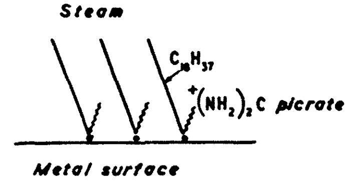
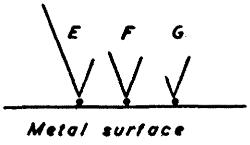


FIG. 3. *Orientation suggested for* (*E*), (*F*), (*G*) (*see text*).



Minimum Effective Concentration of Promoter Solution.—Three typical compounds were examined on brass and copper surfaces. In general, pure copper exhibited dropwise condensation when treated with a solution that was just too dilute to be effective on brass. This was to be expected since the brass surface contained a certain amount of zinc which did not combine chemically with the promoter. The minimum effective concentrations are given in Table 2. Acetone was used as the solvent in each case.

TABLE 2. *Minimum effective concentration* (%) *of promoter for dropwise condensation.*

Surface	(*H*) $C_{12}H_{25}{\cdot}SH$	(*I*) $C_{12}H_{25}{\cdot}Si(S{\cdot}C_2H_5)_3$	(*J*) $C_{18}H_{37}{\cdot}CO{\cdot}S{\cdot}C_{12}H_{25}$
Brass	0·125	0·25	0·25
Copper	0·03	0·125	0·25

With compound (*H*) the ratio of " active " hydrocarbon to bonding sulphur is 1 : 1, whereas with (*I*) it is 1 : 3 and with (*J*) 2 : 1. This suggests that the minimum effective concentration depends on the molecular concentration of either the compound or the active hydrocarbon. With the limited accuracy of the experiment it was not possible to distinguish between these possibilities, but one would expect the latter factor to be the more important. The findings are to be expected, since once the compound is anchored to the surface (by one or more sulphur-containing groups) it is the water-repellent nature (or polarity) of the exposed surface that governs the mode of condensation. This does not mean that there is no advantage in having more than one point of attachment of the compound to the surface. Although proof has not been possible, it is reasonable to assume that the life of a compound on the surface would be greater if there are many points of attachment (at least if breakdown of the surface occurs through rupture of the bond between the active group and the surface).

Effect of Promoter on Oxidised Surfaces.—It was found that at least two promoters had the ability to facilitate removal of surface oxidation from brass. In one life-test, part of the condensing metal surface was oxidised by treatment with aqueous sodium hydroxide solution followed by gentle heating in a Bunsen flame. The whole surface was then thoroughly cleaned with detergent solution followed by water. Dibenzyl sulphide,

$C_6H_5·CH_2·S·CH_2·C_6H_5$, was then applied (1% in ether) to the surface and the test started. The unoxidised surface exhibited perfect dropwise condensation from the start. For the first two days of the test the oxidised part showed only mixed condensation; in 4 days the colour of the surface began to fade from the original dark brown and poor-quality dropwise condensation appeared; after 7 days the surface had changed to a light brown colour and condensation had become identical with that on the unoxidised surface; after about 13 days there was no difference between the two parts of the surface.

Similar changes took place on a badly corroded brass surface, $C_{12}H_{25}·Si(S·C_2H_5)_3$ being used as promoter.

The remarkable action of the promoter in gradually removing the oxide layer from the surface of the metal suggests that the promoter penetrates the layer, thereby facilitating its removal by the steam. That the promoter is responsible for the phenomenon is certain since a clean brass surface that had not been treated with promoter would become heavily oxidised during the normal period of a test, probably owing to dissolved oxygen in the boiler water or to slight penetration of air into the system.

Injection of Promoter Solution into the Steam Supply.—If a 1% solution of promoter in a low-boiling solvent was injected into the steam supply, the efficiency of a promoter to convert the existing condensation from pure filmwise (on a clean surface) into dropwise depended on its structure. Thus, for $C_6H_5·CH_2·SH$ and $C_5H_{11}·O·CS·SK$ only two injections (giving approx. 0·002 g. of promoter) were necessary for a particular condensing surface. Other liquids, *e.g.*, $C_{12}H_{25}·SH$, $HS·[CH_2]_{10}·SH$, and $C_{12}H_{25}·Si(S·C_2H_5)_3$, and the solid $KS·CS·O·[CH_2]_{10}·O·CS·SK$, were relatively effective, requiring only 3—4 injections. However, heavy liquids such as $C_{12}H_{25}·Si(S·C_{12}H_{25})_3$ and $(C_{12}H_{25}·S)_4P_2S_3$, and very insoluble solids such as $C_{12}H_{25}·S·[CH_2]_{10}·S·C_{12}H_{25}$ and $C_{18}H_{37}·O·CS·S·C_{18}H_{37}$, were only slowly effective after about 8—10 injections.

To change the condensate from filmwise to dropwise the promoter must penetrate the initial film of condensate and then adhere to the surface. The heavy liquids and solids, which presumably exist as a suspension in the steam, have difficulty in penetrating the condensate layer. It was observed with these compounds that a small part of the condensing surface initially changed to dropwise condensation, and that this then rapidly spread over the whole surface. This was in contrast to the almost instantaneous change when $C_6H_5·CH_2·S·SH$ or $C_5H_{11}·O·CS·SK$ was used.

If the injection treatment of tubes becomes of industrial importance it should be possible to synthesise efficient promoters incorporating groups which make the compounds sufficiently steam- and water-miscible, in order to facilitate rapid penetration of the condensate. The position of the groups in the molecule would be such that the polarity of the exposed surface was not impaired.

Preparation of Sulphur-containing Derivatives of Undecanoic Acid.—Preparation is described below of several such compounds by methods recorded more fully in Part I.[5] 11-(Carboxymethylthio)- and 11-acetylthio-undecanoic acid were prepared by addition of mercaptoacetic and thioacetic acid respectively to undec-10-enoic acid.

EXPERIMENTAL

S-11-*Carboxydecyl* O-*Ethyl Xanthate.*—11-Bromoundecanoic acid (2·4 g.) and potassium ethyl xanthate (1·45 g.) in hot ethanol gave the *xanthate* (2·15 g.), which crystallised from light petroleum–ethanol in white plates, m. p. 37—38° (Found: C, 55·0; H, 8·8. $C_{14}H_{26}O_3S_2$ requires C, 54·9; H, 8·6%).

The O-*octadecyl analogue*, plates, m. p. 77—78° (from acetone–ethanol) (Found: C, 67·7; H, 11·1; S, 12·1. $C_{30}H_{58}O_3S_2$ requires C, 67·9; H, 11·0; S, 12·1%), was similarly prepared.

11-*Selenocyanatoundecanoic Acid.*—11-Bromoundecanoic acid (5·3 g.) and potassium selenocyanate (3·4 g.) in hot ethanol (25 ml.) gave the *selenocyanato-acid* (5·2 g.), which crystallised from light petroleum–ethanol (6 : 1) as a white microcrystalline powder, m. p. 51—52° (Found: C, 49·5; H, 7·1; N, 4·8. $C_{12}H_{21}O_2NSe$ requires C, 49·6; H, 7·3; N, 4·8%).

11-*Thiocyanatoundecanoic acid*, m. p. 35·5—36° (from light petroleum) (Found : C, 59·3; H, 8·8; S, 12·9. $C_{12}H_{21}O_2NS$ requires C, 59·2; H, 8·7; S, 13·2%), was obtained analogously.

11-[*Acetyl*(*thiocarbamoyl*)*thio*]*undecanoic Acid*.—11-Thiocyanatoundecanoic acid (1·5 g.) with hot thioacetic acid (1 ml.) gave this *product* (1·3 g.) which crystallised from ethanol as very pale yellow needles, m. p. 99·5—100° (Found : C, 52·8; H, 8·0; S, 20·4; N, 4·3. $C_{14}H_{25}O_3NS_2$ requires C, 52·6; H, 7·9; S, 20·1; N, 4·4%).

11-(*Carbamoylthio*)*undecanoic Acid*.—11-Thiocyanatoundecanoic acid (0·2 g.) in ice-cold 96% sulphuric acid (1 ml.) gave the *carbamoylthio-acid* (0·18 g.) which, recrystallised from acetone–light petroleum (3 : 1), had m. p. 140—141° (Found : C, 54·9; H, 8·8; S, 12·6; N, 5·1. $C_{12}H_{23}O_3NS$ requires C, 55·1; H, 8·9; S, 12·3; N, 5·4%).

11-*Mercaptoundecanoic Acid*.—11-Bromoundecanoic acid (2·65 g.) and thiourea (0·76 g.) were heated together in ethanol (10 ml.) for 6 hr. The resulting thiuronium bromide solution was heated with sodium hydroxide (0·8 g.) in alcohol under nitrogen for a further 2 hr. Water (10 ml.) was added, and most of the alcohol removed under reduced pressure. The aqueous solution was treated with concentrated sulphuric acid (5 ml.) and kept at 60° for 2 hr. under nitrogen. The cooled mixture was extracted with ether, and the residue (1·1 g.) after removal of the ether was recrystallised four times from acetone, forming white plates of mercapto-acid, m. p. 93—94° (lit.,[6] 94—95°) (Found : C, 60·2; H, 10·0; S, 14·9. Calc. for $C_{11}H_{22}O_2S$: C, 60·5; H, 10·2; S, 14·7%). [Double the theoretical amount of sodium hydroxide was used in order to convert the product completely into the sodium salt of the acid. Failure to do this resulted in incomplete decomposition of the thiuronium bromide.]

The thiuronium bromide solution with picric acid forms the *picrate*, which crystallises from ethanol in yellow needles, m. p. 177—179° (Found : C, 43·8; H, 5·4; S, 6·8; N, 13·9. $C_{18}H_{27}O_9N_5S$ requires C, 44·2; H, 5·6; S, 6·6; N, 14·3%).

11-(*Dodecylthio*)*undecanoic acid*.—Dodecanethiol (2·0 g.) was heated for 15 min. with sodium hydroxide (0·4 g. in alcohol). 11-Bromoundecanoic acid (2·6 g.) in ethanol was then added, and the mixture heated under reflux for a further 2 hr. The *product* (3·1 g.), which separated as a white solid at 0°, was collected and recrystallised from acetone as white plates, m. p. 61—62·5° (Found : C, 71·0; H, 11·9; S, 8·5. $C_{23}H_{46}O_2S$ requires C, 71·4; H, 12·0; S, 8·3%).

11-(*Carboxymethylthio*)*undecanoic Acid*.—Undec-10-enoic acid (18·4 g.) was warmed till liquid and treated with mercaptoacetic acid (9·2 g.), shaken, and allowed to cool to room temperature; a white solid was formed. An excess of 20% sodium hydroxide solution was added and the mixture stirred. The solid was collected and washed with ice-cold water–acetone (1 : 10), then extracted with ether, and the *product* (26 g.) was recovered and recrystallised from acetone, forming a microcrystalline powder, m. p. 101·5—102° (Found : C, 56·8; H, 8·8. $C_{13}H_{24}O_4S$ requires C, 56·5; H, 8·8%).

11-(*Acetylthio*)*undecanoic Acid*.—Undec-10-enoic acid (9·2 g.) was warmed till liquid and treated with thioacetic acid (3·9 g.). The mixture, which became warm, was shaken until it became solid (20 min.). When cool, the solid was washed with dilute aqueous sodium hydroxide, followed by water, dilute hydrochloric acid, and finally water. The *acetylthio-acid* (12·7 g.) crystallised from acetone in white plates, m. p. 49—50° (Found : C, 60·3; H, 9·4; S, 12·2. $C_{13}H_{24}O_3S$ requires C, 60·0; H, 9·3; S, 12·3%).

The majority of the new compounds synthesised in this work are the subject of B.P. Appln. 9149/55.

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[6] Cohen, *J.*, 1932, 593; Bauer and Stockhausen, *J. prakt. Chem.*, 1931, **130**, 35.