Promotion of Drop-By-Drop Condensation of Steam from Seawater on a Vertical Copper Tube

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A limited number of tests were made of promoters, their method of application, corrosion resistance, etc.

The best promoter found to date is tetrakis octadecyl thio silane $(C_{18}H_{37}S)_4Si$ which differs only in parafinic chain length from $(C_{12}H_{25}S)_4Si$ which was found to be one of the best promoters for drop-by-drop condensation by Blackman and Dewar *(1, 2)*, Hampson *(2, 3)*, and Osment *(4, 5)*. These compounds are nontoxic.

The C_{18} compound appears to be superior to the C_{12} compound in that it is less volatile, lower melting (~34°C), and appears to impart superior oxidation resistance to copper when adsorbed on clean oxide-free metal.

Copper tubes can be rapidly cleaned in place by sulfur dioxide or hydrochloric acid in steam, or, if previously promoted by a thio silane, by treatment first with chlorine gas in steam.

The thio silanes may be rapidly applied as a 1% solution in octanoic acid injected into the sea-water feed. The acid acts as cleaner and poor promoter, allowing the good promoter molecules to contact the metal tube.

The amounts of the best promoters required are in the parts per billion range.

It is well known that heat transfer coefficients in drop-by-drop condensation are much superior to those in film type of condensation, and the mechanism appears now to be fairly well understood (*11, 12*). The major problems preventing commercial application appear to be the following:

1. Most heat transfer equipment involving water vapor condensation is presently designed on the basis of low overall heat transfer coefficients. This equipment cannot take full advantage of drop-by-drop condensation unless the other, frequently controlling coefficients are also markedly improved.
2. In heating aqueous solutions inside tubes the coefficients are considerably better at elevated temperatures. Thus evaporators operating at up to 250°F. or more can benefit much more by employing drop-by-drop condensation than can the usual power plant condenser operating below 100°F.
3. At present drop-by-drop condensation usually requires careful surface preparation of the tubes.
4. High velocity wet steam tends to errode promoters from tubes.
5. Fouling, either by oxidation of the tube or by carry-over of impurities, can cause contamination of the surface. This produces increased heat transfer resistance and usually film type condensation.
6. Many applications, such as seawater conversion, operate on a once through flow of distillate, and hence a drop promoter is required which is long-lived, nontoxic, and cheap to use.

It appears that the application of drop promoters to existing equipment is very likely doomed to failure. For successful economic application it seems that not only the equipment but the process used for cleaning, application, and maintenance (or reapplication) must be carefully worked out.

It is the purpose of this continuing study to overcome many of the obstacles to commercial application of drop promoters, keeping especially in mind application to seawater conversion.

PRELIMINARY WORK

Tests were made several years ago with the following promoters:

1. $(C_{12}H_{25}S)_4Si$ tetrakis dodecylthio silane.
2. $(C_{18}H_{37})_2S_2$ dioctadecyl disulphide.
3. $C_{18}H_{37}OCSSC_{18}H_{37}$ dioctadecyl xanthate.
4. Teflon.

The first three were among those synthesized by Blackman and Dewar (*1, 2*), tested by Hampson (*3*) and Osment (*4*), and recommended by Ede (*6*).

A clean horizontal copper condenser tube was divided into sections, and each was painted separately with a 1% solution of each of the first three promoters dissolved in carbon tetrachloride. Teflon was applied to other sections by spraying or rubbing and then buffing or flaming. Steam was from distilled water; however, the condensate was returned to the boiler. All sections gave good drop-by-drop condensation. The teflon areas deteriorated first. The other three promoters continued to produce drop-by-drop

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condensation, but whereas the areas covered with the disulfide and the xanthate darkened considerably, those covered by the thio silane remained a rather bright copper color. There was appreciable evidence of promoter migration along the tube as well as passage by vapor to and from the boiler.

Based on the preliminary studies and the works of numerous other authors (*1* to *12*), and the fact that most condenser tubing contains copper, it was decided to concentrate on promoters with an affinity for copper. These included the long-chain acids from octanoic through montan wax (a naturally occurring long-chain fatty acid with about twenty-eight carbons derived from some lignites) and the parafinic thio silanes. It was decided not to investigate compounds containing selenium, etc., because of the possible toxic properties, or the permanent coatings like gold or Parylene N now being studied by Erb and Thelan (*7*).

EXPERIMENTAL APPARATUS

The vertical copper condenser tube was arranged to simulate part of a typical stage in a multiple-effect flash evaporator (*13*). The results should however be applicable to either the multistage flash, the usual multiple effect evaporator, or to other schemes.

A flow diagram for the apparatus is given in Figure 1. Filtered, pH adjusted, and degassed seawater at about 500 lb./hr. enters the system through a rotameter. Promoter was injected just after the rotameter or directly into the seawater boiler. The feed seawater passed through the tube side of several preheaters and into the boiler. The boiler was heated by indirect contact with steam contained in copper tubing from a separate external boiler. The steam generated from the boiling seawater entered the condensing section where it condensed on the outside of the copper tube. This copper tube was cooled by circulating distilled water in a closed loop. The condensate as well as the waste brine was sent to drain.

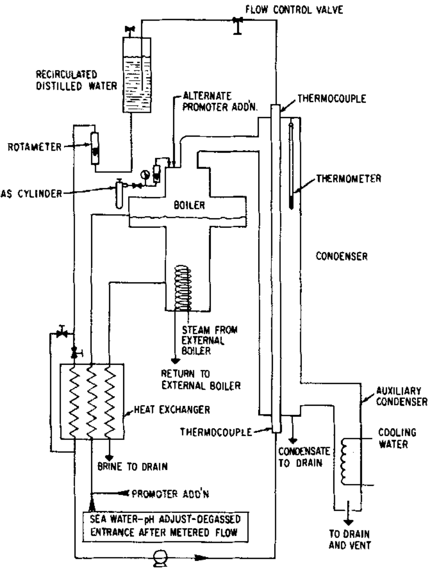

Fig. 1. Condensation apparatus (schematic).

A rotameter was provided to measure the cooling water flow rate, and thermocouples yielded the inlet and outlet cooling water temperatures. The temperature of the steam in the condensation section was measured to 0.01°C. with a mercury thermometer.

The main promoter injection device used was a Whitey Laboratory Feed Pump, Model LP10 capable of pumping from 10 to 160 ml./hr. By intermittent operation on a timer, smaller quantities were pumped. A microsyringe was also used for injection directly into the seawater boiler.

The condenser tube, a $\frac{5}{8}$ in. O.D. copper tube with 0.035 in. wall thickness, was placed in a 3 in. pyrex pipe. The effective length of the copper tube was $56\frac{1}{8}$ in. Normally no advance cleaning or other preparation of the copper tube was carried out. Promotion tests were normally performed only after a tube was cleaned in place and was producing film type condensation.

CLEANING

To make the copper condenser tube ready for application, an effort was made to clean the tube in place without mechanical contact with the tube. If the tube had not been previously promoted with a good promoter a moderately effective cleaning method was to flood the tube with hot (180°F.) acidified (pH 2 to 3) sea water. This rapidly (up to $\sim$1 hr.) removed both cuprous and cupric oxide. Injecting hydrochloric acid gas or sulfur dioxide gas ($\sim$0.1 to 1%) into the steam also was effective. The sulfur dioxide appeared to be somewhat more effective than the hydrochloric acid. Weeks and Hill (*10*) indicate that the rate of solution of cuprous oxide in chloride solutions is about first order in H^+. Neither hydrochloric acid nor sulfur dioxide would remove some of the residues present on some copper tubes.

If the tube had a residue of a good promoter or other organic material such as one of the parafinic thio silanes, a more drastic treatment was required to remove the promoter, as neither sulfur dioxide nor hydrochloric acid appear to attack it. The most satisfactory method was to run in chlorine for a few minutes until film condensation was attained and the tube was darkened considerably. Then follow this by treatment with sulfur dioxide. This usually appeared to strip the tube down to pure copper metal The intermittent addition of chlorine while continuously adding SO_2 to the steam was particularly effective. In one case the final trace of residue only disappeared when a small amount of octanoic acid was added to the steam (by addition to the feed).

Sulfur dioxide, hydrochloric acid, and octanoic acid in the steam, and to a lesser extent the longer-chain fatty acids, appear to react with cuprous oxide to maintain the tube in a clean condition. The clean tube is particularly susceptible to oxidation.

CAUTION

Although chlorine is particularly effective in removing residues from the copper, it appears to accomplish this at least partly by attacking the copper itself causing it to dissolve. Chlorine will tend to accumulate in any inert gas pocket in a condenser and may result in excessive attack of the tubing in this area. The attack appears to be only minimal as long as adequate condenstion is present and the chlorine is not allowed to accumulate.

PROMOTING

After it is cleaned, the tube should be promoted within a few minutes as the unpromoted tube starts to oxidize very rapidly, especially if the concentration of oxygen in the steam is appreciable. This can be partially alleviated by promoting while sulfur dioxide is still being added. Although an oxidized tube can be promoted, oxidation resistance is markedly impaired and the life of the promoter is greatly shortened.

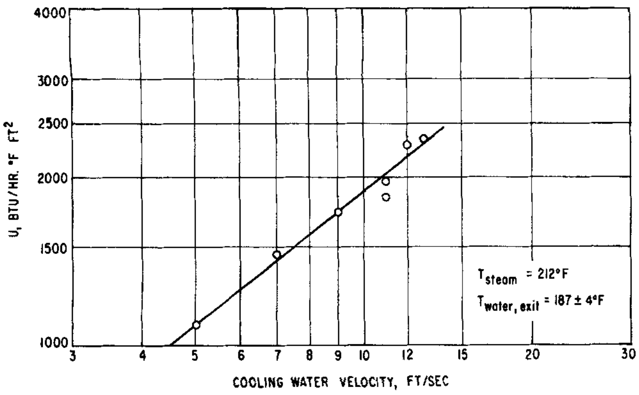

Fig. 2. Overall heat transfer coefficients with high quality drop-by-drop condensation and clean, bright tube.

It was quickly and repeatedly observed that the good long-lived promoters, when introduced into the feed (or steam), would not attack the tube and start promoting (except perhaps at a small spot or two) if the tube was in a good wetting condition and in film type condensation. It is postulated that during film type condensation any promoter molecules that come over in the steam tend to simply come down and remain on the water-steam interface and get swept away. They never get down to the metal. Other evidence for this is

1. The good promoters are extremely insoluble in water.
2. The good promoters tend to suppress foaming of seawater, indicating that they tend to concentrate at the vapor-liquid interface and to remain there unless contacting metal.

Thus to promote rapidly with a good promoter, it is necessary to also add a rapid promoter with appreciable solubility in water which will cause the liquid film to break up and allow the good promoter molecules to contact the metal surface.

One such quick but poor promoter which is also a cleaning agent is octanoic acid. This acid will dissolve (after heating to about 50°C.) over 5% of the parafinic thio silanes but only about 0.1% montan wax.

The solution of the promoter(s) was normally injected into the seawater feed. In the case of octanoic acid, it was most effective when the seawater had a pH not over 4.5. At high pH values, the acid probably exists largely as the ion in seawater and does not appear to distill as readily.

Iso-propyl alcohol, kerosene, coconut oil, and others were also tried because of their low cost.

FOAMING

Coconut oil (0.1 to 1.0 p.p.m.) had marked anti foaming activity. Montan wax and the thio silanes also showed some anti foaming activity. On the other hand, excessive amounts of pure octanoic acid tended to increase foaming of seawater. The solution of the thio silanes in octanoic acid was a slight foam depressant.

PROMOTION RESULTS

The results are summarized in Table 1. The criterion of quality of drop-by-drop condensation noted is that suggested by Osment et al. (5) who show photographic samples. It will be noted that the best results were obtained from montan wax and the parafinic thio silanes. The heat transfer coefficients reported are typical values and are considered accurate to ±100 B.t.u./(hr.) (sq. ft.) (°F.) for the condition described. Typical outside coefficients calculated for good quality drop-by-drop condensation were ~10,000 B.t.u./(hr.) (sq. ft.) (°F.) but were very uncertain and could easily have been twice this figure. Any fouling resistance was included with the outside coefficient. It should be noted that the value of the overall coefficient is 1,700 B.t.u./(hr.) (sq. ft.) (°F.) for the lower flux (14,000 B.t.u./(hr.) (sq. ft.) in the case of drop-by-drop condensation with $(C_{18}H_{37}S)_4Si$. This is more nearly in the range to be expected in seawater conversion equipment. This is higher than the 1,500 reported at the same water velocity for the high flux value mainly because of the somewhat higher cooling water temperature. Inside coefficients were calculated from the typical Dittus-Boelter equation for flow of pure water on the inside of a pipe. The effect of cooling water velocity is shown in Figure 2. The higher coefficients given at the higher velocities reflect not only the effect of velocity but also the fact that the average cooling water temperature was somewhat higher at the higher velocities.

Montan wax: this promoter was most successfully added as a saturated solution (~0.1%) in octanoic acid, although once drop-by-drop promotion is established it is thought that intermittent (~every hour) or continuous

TABLE 1. SUMMARY OF PERFORMANCE OF DROP-BY-DROP PROMOTERS IN CHRONOLOGICAL ORDER

Promoter	Solution	How injected	Typical U*	Comments
Silicone Dow Corning 1107	1% in isopropyl alcohol	20 ml./hr. for 5 hr.		Small amount of very poor quality drop-by-drop extending about one fourth way down condenser tube.
$(C_{12}H_{25}S)_4$ Si	1% in kerosene	20 ml./hr. for several days		About 10 hr. required to produce 100% drop-by-drop. Excellent quality.
$(C_{12}H_{25}S)_4$ Si	0.1% in kerosene	20 ml./hr. for 8 hr.		Maintained excellent drop-by-drop obtained above. Condensate smells like kerosene.
Octanoic acid	1% in isopropyl alcohol	45 ml./hr. for 3½ hr.		Very poor drop-by-drop covered tube. Cleaned residual oxide off tube.
Stearic acid	1% in isopropyl alcohol	45 ml./hr. for 2 hr.	1,100	Slightly better than octanoic acid.
Oleic acid	1% in isopropyl alcohol	65, 45, 25 ml./hr. ea. for 1 hr.	1,300	Slightly better than stearic acid but still of poor quality.
Cupric oleate	Sat'd sol. in isopropyl alco.	25 ml./hr. for 2½ hr.	1,400	Slightly better than oleic. Still poor quality. One third of tube reverted to film type 10 min. after ceasing injection.

Promoter	Solution	How injected	Typical U*	Comments
Montan wax	Seawater, contacted sol'n. wax in octanoic acid	45 ml./hr. for 5½ hr.		No drop-by-drop condensation. Montan wax extremely insoluble in seawater.
Montan wax	Sat'd. sol'n. (~0.1%) in octanoic acid	Various rates intermittently	1,500	Excellent drop-by-drop. Would last ~2 hr. after stopping injection.
Montan wax	Pure wax	Passed feed seawater through packed bed of wax		No drop-by-drop condensation, wax too insoluble.
Montan wax	Sat'd. sol'n. in isopropyl alcohol	65 ml./hr. for 1½ hr.		Very poor drop-by-drop. Did not seem characteristic of montan wax.
Montan wax	Sat'd. sol'n. in conc. H_2SO_4	65 ml./hr. for 1½ hr.		Very poor drop-by-drop. Wax may have been decomposed.
Montan wax	Sat'd. Sol'n. in oleic acid	45 ml./hr. for 3 hr.		Good drop-by-drop 30 min. after start. Like wax in octanoic except cleaning not as good.
$(C_{12}H_{25}S)_4Si$	0.1% in actanoic acid	27 ml. in 35 min.	1,500	Excellent to good drop-by-drop condensation continued for 86 hr. No new promoter added. About one fourth film type at end. Tube rather clean after standing over weekend.
Montan wax + $(C_{12}H_{25}S)_4Si$	0.1% in coconut oil containing 10% octanoic acid	To give 1 p.p.m. coconut oil in seawater	900	Excellent foam suppression. Promotion started at top and slowly spread to three eighths of tube after 48 hr. Eighteen more hours no change.
$(C_{12}H_{25}S)_4Si$	1% in octanoic acid	6 ml. intermittently injected over 1 hr.	1,500	Very good drop-by-drop. Some deposited on oxide is inferior to that on clean metal.
Montan wax	Liquid wax at ~100°C.	0.033 cc. into boiler in increments		Almost no drop-by-drop.
Montan wax	0.1% in octanoic acid	6.9 cc. at rate corresponding to 4 p.p.m. octanoic acid		After 6 hr. about 40% of tube drop-by-drop.
Removed tube and cleaned by scrubbing with NH_4OH—$(NH_4)_2CO_3$ sol'n. Replaced and flooded with acidified seawater. Gave 100% film type				
$(C_{18}H_{37}S)_4Si$	1% in octanoic acid	Add 20 ml. intermittently over 1¼ hr.	1,500 (1,700)±	After ~3 ml. 95% good drop-by-drop. After 20 ml. 99% excellent drop-by-drop. Ran during days only for 49 hr. condensing. 95% excellent at end. Almost no tarnishing after 12 days including two weekends.
Octanoic acid	Pure acid	0.1 ml. directly into boiler		Poor short-lived drop-by-drop on entire tube.
$(C_{18}H_{37}S)_4Si$	Pure liquid	0.03 ml. directly into boiler		Only two very small spots of drop-by-drop condensation appeared.
Lauric acid	Pure acid heated to liquefy	0.1 ml. directly into boiler		Almost exactly like octanoic, perhaps a little longer lived.
$(C_{18}H_{37}S)_4Si$	1% in octanoic acid	4 ml. in 1½ min.	(1,700)±	100% excellent drop-by-drop in 3 min. Tube had been carefully cleaned in place in ~1 hr. after oxidizing in air using a little chlorine to remove residual promoter followed by sulfur dioxide (all in steam). 100% clean and film type before promoter add'n. After 100% drop-by-drop, promoter was then 100% removed by chlorine to film type in 1 min. Tube darkened. Sulfur dioxide add'n. produced pink 100% film type tube in 2 min. which oxidized rapidly on standing in air.
$(C_{18}H_{37}S)_4Si$	1% in octanoic acid	0.1 ml. added directly to boiler		Chlorine-sulfur dioxide cleaning before add'n. Excellent drop-by-drop almost instantly (~10 sec.) on lower half of tube. Good on top half.
$(C_{18}H_{37}S)_4Si$	1% in octanoic acid	1.0 ml. directly into boiler		100% excellent drop-by-drop condensation; good oxidation resistance.
$C_{18}H_{37}SH$	1% in octanoic acid	1.0 ml. directly into boiler		Chlorine-sulfur dioxide cleaning before add'n.** 100% excellent drop-by-drop condensation. On standing in air, oxidation resistance inferior to thio silanes.

* For comparison, $U_{\text{film type}} = 700$ B.t.u./(hr.)(sq. ft.)(°F.) These represent typical values corrected to a flux of ~ 42,000 B.t.u./(hr.)(sq. ft.) cooling water velocity 7 ft./sec., and are for outside surface of tube.

± This value is at a reduced but more nearly typical flux of ~14,000 B.t.u./(hr.)(hq. ft.). The film type coefficient is ~ 900.

** The procedure involving cleaning with sulfur dioxide with short bursts of chlorine and direct addition of about 1 ml. of 1% thio silane in octanoic acid was repeated many times with the same result. Oxygen must be kept away from the tube after cleaning and before promotion or the promoter will deposit on the oxide, resulting mainly in poor promoter life and decreased oxidation resistance. Traces of chlorine must not be allowed to contact the promoted tube or the promoter will be partially removed and oxidation will proceed.

injection of the molten wax (m.p. ~80 deg.) into the hot seawater would suffice, although this has not yet been conclusively demonstrated. The amount of wax used was ~100 ppb of distillate, although the amount required may be somewhat larger than this in the absence of octanoic acid. Although a solution in octanoic acid is quite satisfactory for initial feeding, it would seem unsatisfactory for continued operation both for costs and possible toxic problems of any copper salts formed.

It was further observed that, on standing overnight in a moist seawater atmosphere, montan wax offered only a fair degree of corrosion protection, although better than the other organic acids but not nearly as good as the parafinic thio silanes.

Parafinic thio silanes: the two compounds tested had the general formula $(RS)_4Si$, with R being 12 and 18 carbons long, respectively. These gave excellent drop-by-drop condensation but, like montan wax, required solution in a poor promoter like octanoic acid to effect initial rapid promotion. A total octanoic injection rate of from 100 to 800 p.p.m. (20 to 160 ml./hr.) for a few minutes is adequate to fully promote the tube if a 0.1 or 1% solution is used and the tube is clean to start with. Direct addition of 1 ml. of 1% solution to the boiler is equally effective.

Whereas the life of montan wax appeared to be of the order of 1 hr., the thio silane compounds appeared to have lives of at least 50 hr. without further promoter addition. The amounts of these thio silanes used were calculated to be from 1 to 10 ppb of feed, although there is some evidence that even less than 1 ppb might be effective if properly managed.

The octadecyl compound appeared to be somewhat superior to the dodecyl. Its lower melting point, 34°C., as compared with 44°C. for the dodecyl, is desirable. It also was estimated to have a vapor pressure ($\sim 10^{-5}$ mm. mercury at 100°C.) one to two orders of magnitude lower than the dodecyl compound. This should improve its life and yet is still high enough so that it distills readily onto the tube.

OXIDATION RESISTANCE

Except when the copper tube was coated with the parafinic thio silane promoters the copper tube would discolor (oxidize) quite markedly on standing several hours over seawater.

With $(C_{12}H_{25}S)_4Si$, oxidation was marked only on standing over a weekend, whereas with $(C_{18}H_{37}S_4)Si$, daily use and standing each night, including two weekends, resulted in barely perceptable tarnishing of the copper surface.

The oxidation resistance imparted to the copper appears to be from several basic causes:

1. The strong bonding of the sulfur to both the silicon and the copper (chemisorbed) appears to inhibit oxidation.
2. The presence of the hydrocarbon as well as the sulfur atoms appears to keep the surface dry even when stored over seawater.
3. The long-chain hydrocarbon ends, when closely packed on the surface, would offer appreciable diffusion resistance to oxygen.
4. The low inherent volatility of these compounds, together with their strong adsorption, appears to allow them to remain on the surface for long times without being removed.

Where hydrocarbon chains were not closely packed, oxidation resistance was also implied from the following observation. After being run for quite some time with these compounds, the normal excellent drop-by-drop condensation would change to low grade drop-by-drop or film type at spots on the tube (usualy near the bottom and near a defect in the film); however, the tube remained clean and bright overnight. There appeared to be some promoter present. Water formed somewhat flat irregular drops on this surface when it was not flooded by condensate, and the surface looked like bare metal. This would seem to indicate that the most important single factor in preventing oxidation is keeping all exposed copper atoms covered with hydrocarbon (or S-Si) groups.

The promoters will attach themselves to oxidized spots but when attached this way they have much more limited life, and much poorer oxidation resistance was observed. Traces of chlorine gas quickly damage the promoters.

MOLECULAR ARRANGEMENT

To be most effective the amount of promoter added must be such that the concentration (film pressure) is sufficient to form a close-packed monolayer of molecules standing on end. It seems likely that three of the sulfur atoms are attached, but mobile, to the copper surface by chemical or physical adsorption. The closely-packed hydrocarbon chains form the water repellent surface.

As promoter is lost by erosion or evaporation, there is evidence that the promoter molecules migrate and also tend to lay down on the surface. This accounts at least partially for the fair oxidation resistance imparted to the copper by these molecules.

TOXICITY

It appears that montan wax, because of its similarity to the other long-chain fatty acids and its extreme insolubility, should be nontoxic, although no tests were made to confirm it.

A toxicity test was made of $(C_{12}H_{25}S)_4Si$ by the Bio-Technics Laboratories, Inc. Tests up to three weeks on mice, rats, and rabbits were made for oral, intraperitoneal, subcutaneous, skin irritation and intravenous toxicity. No toxicity was found. Their stated conclusion is: "The product submitted for analysis and identified as tetrakis (dodecane-thio) silane on the label appears to be nontoxic when orally ingested and when injected subcutaneously as well as when applied topically using mice, rats, and rabbits. Intravenous injection of the water extractables was also nontoxic. Results indicate no acute toxicity over a range of varying dosages."

Based on this it seemed reasonably safe to assume that for the amounts which might be present in water from a plant using this promoter, certainly it should be nontoxic to humans. It seems reasonable to predict that $(C_{18}H_{37}S)_4Si$ should be equally nontoxic.

Based on present prices of ~70¢/lb., the cost of montan wax required would be about 0.06¢/1,000 gal. of product.

At this time the thio silanes are laboratory curiosities and their prices are high, ~$190/lb. for $(C_{12}H_{25}S)_4Si$. If one estimates that with reasonable production since the ingredients are cheap and only a few simple steps are required, the cost would be reduced to about $25/lb., and that 10 parts per billion, based on product, would be required, one comes out with a cost of 0.2¢/1,000 gal. The cost of sulfur dioxide and chlorine required are estimated to be in this same order of magnitude.

Present evidence indicates that when properly applied, in equipment designed for their use, the use of drop promoters should result in a saving of several cents per thousand gallons.

EQUIPMENT DESIGN

Based on present knowledge, it appears that the following points should be considered in design of equipment intended to utilize drop-by-drop condensation.

1. Because heat transfer coefficients are much higher with this type of condensation, economic optimum design will require that other heat transfer coefficients also be large. This will cause high velocities to be specified inside tubes and will indicate a distinct advantage of using high conductivity tubes.
2. The design must prevent impingement of high velocity entrained liquid on the condensing surface.
3. Materials which will tend to give rise to carry-over of fouling materials, like ferric hydroxide, should be eliminated; that is iron pipes should not be used in vapor piping.
4. The water vapor must be kept as free of oxygen as possible; that is, leaks in vacuum stages and lines should be eliminated, and entering seawater should be oxygen free.
5. The tube material or the promoter chosen must minimize oxide formation from the metal of the tube.
6. Inert gases such as nitrogen and carbon dioxide should be prevented from entering the system as much as possible and should be well vented from the condensing areas. No inerts pockets should be allowed to exist.
7. The equipment should incorporate means for easy cleaning and repromoting condensing tube surfaces.

PROCEDURES

1. The simplest and cheapest method of tube cleaning appears to be by addition of appropriate cleaning agents to the condensing steam. Sulfur dioxide is quite effective in removing oxides from copper tubes. An occasional burst of chlorine may also be helpful in removing insoluble residues but should be applied with caution.
2. Initial promoter application shoull be done quickly to minimize promoter loss, increase production, and reduce costs. This will probably require a two-component promoter such as $(C_{18}H_{37}S)_4Si$ in octanoic acid.
3. The promoter should be added directly to the seawater feed or possibly directly into the individual stages to be promoted. The promoter will be carried over with the vapor to the condensing surface.
4. Maintenance may require intermittent cleaning and further addition of promoter.

For application to sea water conversion perhaps the most critical property of promoters and other materials used is that they be nontoxic in the amounts required. The thio silanes, probably montan wax, sulfur dioxide, and chlorine, and even possibly octanoic acid appear to meet this requirement.

Furthermore, the amounts required should be such that the cost reduction by increased production exceeds the cost of promoters, their application, and maintenance.

OTHER POSSIBLE PROMOTERS

On the basis of present evidence, it appears that the best adsorption characteristics on copper surfaces are those molecules containing sulfur preferably attached to silicon.

The hydrocarbon tail is used to provide the hydrophobic character for drop promotion.

It is well known that fluorocarbons also have excellent hydrophobic character, probably even superior to the hydrocarbons. Hence it may be that if the hydrocarbon tail is replaced with a fluorocarbon, an even superior promoter molecule will result. The latter might also be somewhat more resistant to corrosion and fouling.

SUMMARY

Montan wax and especially the parafinic thio silanes appear to show promise as promoters for commercial application of drop-by-drop condensation to seawater conversion.

The best promoter tested was tetrakis (octadecyl thio) silane $(C_{18}H_{37}S)_4Si$.

These promoters should be added only to clean tubes. Acidified seawater, sulfur dioxide, or hydrochloric acid gas (in steam) will normally remove the oxides of copper. Chlorine will remove $(C_{18}H_{37}S)_4Si$. The chlorine treatment followed by sulfur dioxide (in steam) results in a clean copper tube with film-by-film condensation.

To effect rapid initial promotion these good promoters must be added along with a substance which itself induces quick (although not necessarily good) drop-by-drop condensation such as octanoic acid.

The promoters were added by injection directly into the feed seawater. Montan wax, because of its higher melting point, should probably be added to seawater above 80°C. Low temperature stages in an evaporator may require direct injection of the dual promoter into the stage.

Time between required injections for montan wax is measured in hours, whereas for thio silanes it is measured in days.

At a cooling water velocity of 7 ft./sec., drop-by-drop condensation roughly doubles the overall coefficient on a vertical ⅝ in. copper tube.

Projected costs appear to be in the order of a fraction of a cent per thousand gallons of product.

Tests have only been conducted on copper but should be somewhat applicable to copper bearing alloys.

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