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HIGH-TEMPERATURE LIQUID HEAT SYSTEM

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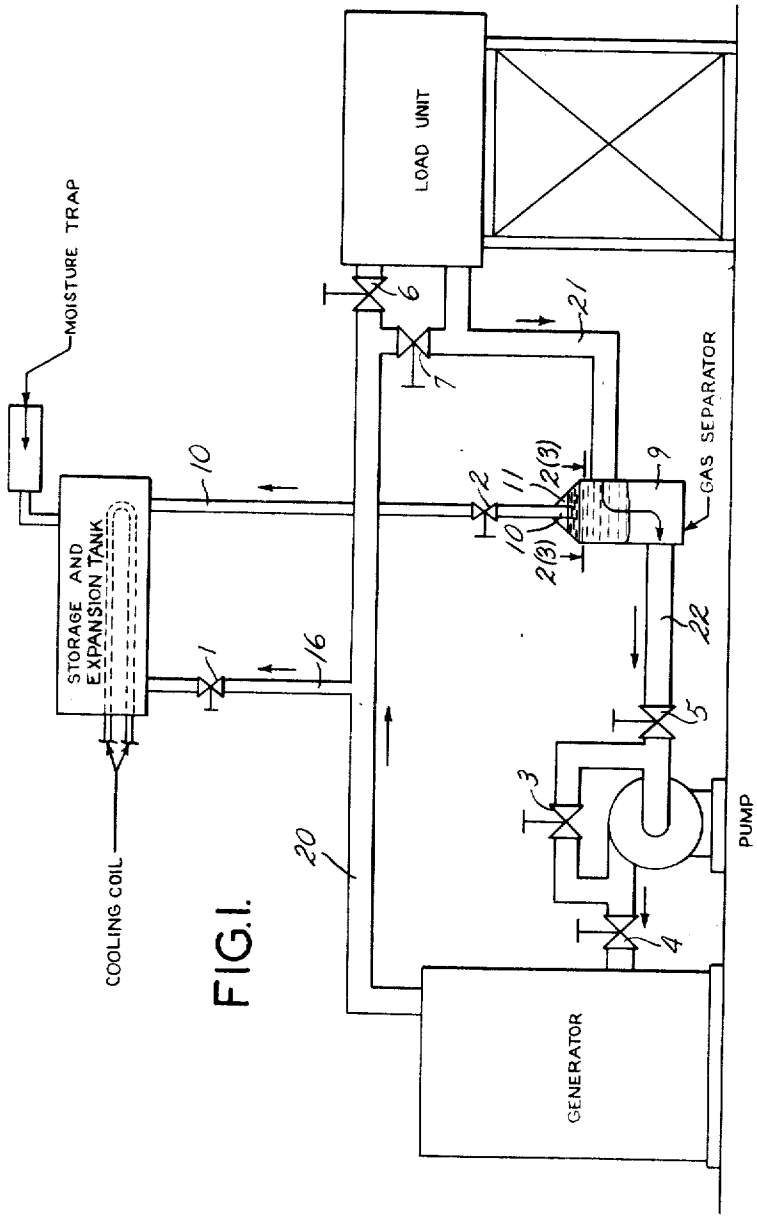

FIG. 1.

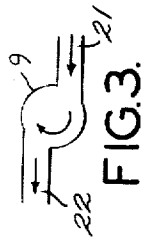

FIG. 3.

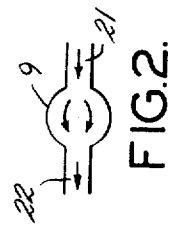

FIG. 2.

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HIGH-TEMPERATURE LIQUID HEAT SYSTEM

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3 Claims. (Cl. 237—63)

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This invention relates to a process and apparatus of utilizing heat energy through the use of a circulating liquid, and more particularly to heat transfer systems and to a process of applying heat by contacting the same with a heat transfer liquid.

Certain types of heat transfer systems are designed to convey heat to a surface to be heated through circulation of liquid at an elevated temperature. The liquid necessarily has a high boiling point which is substantially above the operating temperature. Such a system normally comprises a generator or boiler for heating the liquid, a load unit containing the material to be heated, means for circulating the liquid through the system, such as a pump, and a storage or expansion tank for receiving liquid as a result of expansion of the liquid during heating.

Such a simple system gives no difficulties, provided the heat transfer liquid is stable and remains in the liquid state throughout the system. If the static head pressure is above the vapor pressure of all the components of the liquid, the heat transfer medium remains in the liquid phase. The use of such a system employing a heat transfer medium in the liquid phase is to be distinguished from a system in which the heat transfer medium is vaporized and the vapor used for heating.

If the temperature of the liquid is close to the boiling point of any component, it may not be possible to maintain a pressure necessary to prevent vaporization of at least a portion of the liquid. When the temperature level approaches the boiling point of any component of the liquid at the system pressure there is always the danger of vapor formation. In addition such liquids often tend to break down due to cracking, dissociation or other types of reaction when maintained at high temperatures over long periods of time so as to liberate components of lower boiling point.

When vapor formation occurs for any reason, vapor lock in the system may result. The vapor is most apt to form at the point of lowest pressure which is usually at the inlet side of the pump. If vapor lock forms in the pump there is a resultant failure of circulation of the liquid throughout the system. After circulation ceases, decomposition of the liquid at certain points due to overheating is accelerated, with formation of more vapor and often with the formation of resins or other solids which are precipitated in the lines.

When the difficulties described above are

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caused by a decomposition of the liquid, the formation of lower boiling components may be the result of a substantially irreversible reaction. In such cases the low boiling components serve no function in the system and their presence is undesirable for the reasons explained heretofore. The cracking of hydrocarbon oils is typical of this type of reaction.

The formation of lower boiling components may be the result of dissociation or a reaction that is reversible at least to some extent. In such cases it is desirable to maintain the lower boiling components in contact with the liquid to repress the dissociation and to permit the reassociation of the components under conditions where this is favorable. The dissociation of organic silicates is illustrative of this type of liquid. Tetra-aryl silicates, for example, upon prolonged heating at a high temperature, liberate phenols which boil below the temperature at which a system using tetraphenyl silicate would ordinarily be operated. If the liquid is kept in contact with the phenol, the dissociation to liberate the phenol is repressed to some extent and the phenol may reassociate with the liquid at least in part, under conditions favorable for such reassociation, such as when the liquid is cooled. Some decomposition may take place which represents reactions which are not reversible, such as the formation of hydrocarbons. However, by the judicious selection of a tetra-aryl silicate in relation to the temperature of operation, irreversible dissociation or decomposition reactions may be minimized if any phenol liberated is kept in contact with the liquid in the system.

The problem is aggravated if the tetra-aryl silicate is or contains tetracresyl silicate. Use of such compositions has been suggested because of their high boiling points and low freezing points. Mixtures containing 20% tetracresyl orthosilicate and 80% tetraphenyl orthosilicate have been recommended in the patent literature. Experience has shown that such a mixture does not have a sufficiently low freezing point and consequently most commercial mixtures contain approximately 40% tetracresyl orthosilicate and 60% tetraphenyl orthosilicate.

It has been found that when pure tetracresyl orthosilicate or mixtures thereof with tetraphenyl orthosilicate are subjected to high temperatures, say of the order of 700° F., over a period of several months, even in a closed system wherefrom neither liquid nor vapor can escape nor air, moisture or impurities enter, sub-

stantial amounts of lower boiling products are formed. These products are largely low-boiling substances and include phenol, cresol, which may reassociate under suitable conditions and benzene, toluene, xylenes and other hydrocarbons which are not thought to reassociate. While a system employing such a liquid initially may operate for a time at the desired high temperature, it may be necessary during operation over a period of months gradually to reduce the operating temperature to prevent vapor lock of the pump due to the liberation of vapors at higher temperatures.

It has now been determined that if vaporous low boiling components of any liquid are separated before appreciable quantities thereof reach the pump the useful life of the system can be prolonged. Accordingly, it is an object of the present invention to provide a process of separating gaseous low-boiling components from heat-transfer liquids in normal use, and to provide a heat transfer system including means for separating gas from said liquid in normal course of circulation thereof through the system.

It is a further object of the invention to provide a heat transfer system of the type described including a storage means, and a gas separator and means for discharging gas therefrom into the storage means.

It is another object of the invention to provide, in a heat transfer system, means for continuously separating gases from liquids, and accumulating them in the liquid state in another part of the system.

It is a further object of the invention to provide a process or a system in which the lower boiling components are separated and condensed, and despite the separation of these lower boiling components from the liquid so as to prevent vapor lock in the system to maintain them in contact with the liquid so as to minimize dissociation and to permit reassociation of the separated components under favorable conditions. To this extent it is an object of the invention to maintain a liquid in the system in chemical and physical balance.

The heat transfer system in accordance with the invention comprises, in combination, means for heating the liquid, means heated by the liquid, means for circulating and conveying the liquid from the heating means to a means to be heated, storage means for receiving fluid (liquid or gas), from and returning liquid to the system, and means for separating gas from said liquid and discharging it into said storage means.

The system may be operated vented to the atmosphere in which case the pressures in the system are confined to the static head in the lines and the kinetic heads developed by the circulation. Also the system may be operated so that a positive pressure is exerted upon the system, in excess of atmospheric pressure, i. e., the system is operated under a superatmospheric pressure. In either case, when the pressure upon the system is sufficiently in excess of the partial pressure of low-boiling substances in the circulating liquid to cause a substantial amount of said substances to be retained in the liquid phase decomposition of the liquid is thereby inhibited. The pressure need not, although it may, be sufficient to retain substantially all low-boiling substances, including decomposition products, in the circulating liquid. The presence of a substantial amount of such substances appears to suppress the decomposition reaction. When the partial

pressure of low-boiling substances in the circulating liquid exceeds the pressure upon the liquid, whether operating at atmospheric pressure or under a positive pressure, such gases are permitted to escape from the liquid, although not from the system, and are collected, for example, in the storage tank, wherefrom they may be returned to the system as desired, for example, when the operating temperature of the system is lowered or liquid is withdrawn from the system at another point.

The process of the invention therefore contemplates not only the step of removing low-boiling components from the heat transfer liquid, in order to prevent their accumulation to a concentration at which vapor lock will occur, but also the step of maintaining the system under a positive pressure to retain in the liquid an amount of low-boiling components liberatable in decomposition of the liquid in use sufficient to inhibit decomposition thereof, while permitting low-boiling components in excess of such amounts to escape from the liquid, preferably accumulating them in another part of the system.

Another important aspect of the invention is the relative location of certain elements. The heat generator and the material to be heated (load) are connected so that the heated liquid may be conveyed to the load and the cooled liquid returned to the heat generator. The circulator, generally a pump, may be located in the line leading from the heat generator or in the line returning the liquid to it. For reasons to be explained later, the latter is usually preferred. The gas separator, however, is invariably located adjacent the circulator on the inlet side thereof, as this is the point of lowest pressure in the system and the separation of gases at this point gives the greatest assurance against failure of the system due to vapor-lock in the circulating means.

One embodiment of heat transfer system in accordance with the invention is shown schematically in Fig. 1.

Schematic representations in cross section of two gas separators in accordance with the invention are shown in Figs. 2 and 3, respectively.

The system of Fig. 1 comprises a generator, a storage and expansion tank which is provided with a cooling coil and a moisture trap, and is connected to the remainder of the system at two points, a load unit which comprises the surface to be heated, a gas separator, and a pump for circulating liquid through the system in the direction of the arrows.

The liquid flow through the system is controlled by valves 1 to 7, inclusive.

The gas separator in the form illustrated is a stationary upright tank and comprises a separation chamber 9 connected to inlet and outlet pipes 21 and 22, respectively. A pipe 10 connects the upper portion of chamber 9 with the expansion tank, the flow of liquid and/or gas through the pipe being controlled if desired by the valve 2. The lower end of the pipe 10 defines the lower end of a gas-receiving portion 11, which comprises the upper portion of the chamber 9. Gas discharged from the liquid circulated through the chamber 9 tends to rise therein and to collect in the upper portion 11 of the chamber 9. The gas separator may take various forms. It may simply be a closed tank with an inlet and outlet as shown in Figure 2. Only slight agitation will be noted if the ar-

rangement thereof is as shown in Fig. 2. The gas accumulates in the top of the tank and passes up through the pipe 10. Alternatively the inlet and outlet may be arranged as shown in Fig. 3 so that the liquid passes through the tank in a whirling motion. This facilitates the separation of the gas at the center, near the entrance to the pipe 10. Other means providing vapor separation, such as baffles, may also be employed. The vent pipe 10 may also be lowered to provide a greater gas-liquid surface for the removal of bubbles formed at the surface.

When the system is started up valves 1, 2, 4, 5 and 7 are opened and valves 3 and 6 closed. Heat transfer fluid of the type which liberates low-boiling substances is charged into the system until it is filled. The burner in the generator is then turned on and the liquid heated while circulating it with the aid of the pump until the operation temperature has been reached. As is apparent from the drawing, liquid circulates, in order, through the line 20 from the generator, by passing the load unit through valve 7, then through line 21 to the gas separator and the chamber 9, through line 22 to the pump, and back into the generator. As the liquid is heated it expands, and the excess is allowed to flow from line 20 through line 16 into the storage tank. After the liquid has reached operation temperature and expansion is complete, valves 1 and 7 are closed and valve 6 is opened. Circulation through the load unit is then begun.

In the normal course of operation decomposition of the heat transfer fluid takes place, liberating low-boiling substances. As the liquid passes through the chamber 9 of the gas separator, gaseous low-boiling substances pass upwardly through the liquid and collect in the upper part of the separator 11. The pressure of gases builds up, and the level of the liquid in the separator is lowered in consequence by forcing some of the liquid up into the pipe 10 until finally the partial pressure of gas in the chamber equals the static head of pressure of the liquid in the pipe 10. At this point the level of the liquid is just at the lower end of the pipe 10. Thereafter as gas continues to collect in the chamber 11, the pressure therein exceeds the static head of pressure in the pipe (and therefore in the system) once the liquid level is lowered below the end of the pipe, and gas escapes upwardly through the pipe 10 into storage tank. There the gas is condensed by the cooling coils if atmospheric cooling is not sufficient.

The portion of the liquid which is thus transferred to the storage and expansion tank is replaced by liquid from it. Thus the liquid in the tank is in equilibrium with the liquid in system, and the separator functions to replace the high boiling liquid initially in the tank by low boiling components developed during use.

Gradually during operation, as heat transfer liquid decomposes, the concentration of liquid low-boiling substances in the storage and expansion tank increases. Even though low boiling components in liquid form return to the system through the pipe 10 they will at once be vaporized when they meet the hot liquid in the chamber 10 and will be removed. The liquid returning to the system in the pipe 10 will be a mixture of high and low boiling components. The high boilers will be added to the system liquid and the low boilers will again be separated. In this way the low boilers are in contact with the liquid in the system and are available for such reassociation reactions, or such repression of decomposition as occurs, depending on the liquid and the temperature of operation.

In the case of tetra-aryl orthosilicates, it is desirable to have the phenol present in the liquid as this minimizes decomposition and represses dissociation. Its presence is objectionable only when it causes a circulatory failure of the system. In the system of the invention, the liquid always has the maximum amount of phenol that can be tolerated under any conditions of operation. For example, if the conditions shift so that a larger amount of phenol can be present in the liquid, the phenol from the storage tank will return to the liquid through pipe 10. Any surplus is retained in readiness for reassociation with the liquid under conditions which are suitable. Thus the chemical composition of the liquid adjusts itself to the requirements of the system, and to this extent the system is in chemical as well as in physical balance.

When the expansion and storage tank contains only low boilers the system can no longer operate to remove low boilers because the liquid removed as a gas through pipe 10 is the same as that being returned as a liquid. In such event the liquid in the tank may be exchanged for a fresh portion of heat transfer liquid without interruption of the operation of the system. By this expedient the liquid's useful life may be prolonged indefinitely. No difficulties such as reduced pumpability are experienced.

When the system is closed down, the heat transfer liquid will, of course, cool and therefore contract to a considerable extent. As contraction thereof proceeds, condensed low-boiling substances will flow downwardly through the pipe 10 into the circulating system proper. This will increase the concentration of low-boiling substances in the circulating liquid. If the liquid is one in which the low-boiling components reassociate chemically, this reassociation can take place readily. When the system is again started up, the low-boiling substances if present or if generated, will be returned to the storage tank in due course of operation.

The apparatus of the invention shown schematically in Fig. 1 may easily be adapted for use at superatmospheric pressure. Pressure is applied to the system and kept constant by a pressure regulator-vacuum relief set up connected to the storage tank, pressure being exerted upon the surface of liquid in the tank and thereby applied to the system. In other respects the system is similar to that of Fig. 1, and its operation is similar. Since, however, the modified system is under a superatmospheric pressure, gas collected in portion 11 of the separator must accumulate to a higher vapor pressure than in the unmodified apparatus of Fig. 1 before liquid therein is depressed to below the level of pipe 10 and gas can escape to the storage tank. The higher gas pressure in the portion 11 tends to inhibit escape of gas thereinto from the heat-transfer liquid, so that a higher concentration of low-boiling components is maintained in the heat transfer liquid.

As the system is started up under superatmospheric pressure and decomposition of the heat-transfer liquid begins, low-boiling decomposition products are accumulated therein until the partial pressure thereof equals the pressure exerted on the system. Thereafter gaseous decomposition products escape freely from the liq-

uid through the gas separator, as when the system is operated at atmospheric pressure.

As illustrative of the advantages of the system of the invention as compared with the conventional system, a system was operated identical with that shown in Fig. 1 except that it did not contain the gas separator 9 and vent pipe 10 connecting with the storage tank. The system was charged with a tetra-aryl silicate consisting essentially of 60% tetraphenyl silicate and 40% tetracresyl silicate. The liquid was heated up to a temperature of 801° F. and as it was operated at this temperature, vapor lock in the pump took place after only a few hours of operation. The temperature was gradually decreased and maintained at the maximum at which vapor lock did not occur. After operating the system over a period of days, the maximum temperature maintainable was 480° F. Although the low-boiling decomposition products in the liquid at this time amounted to only a few percent, this small amount of low boiling components was sufficient to require the lowering of the operating temperature in order to maintain circulation in the system. The gas separator was then installed, as shown in Fig. 1, and connected to the storage and expansion tank by means of the vent pipe 10, as illustrated in Fig. 1. The system was again put into operation and the temperature gradually increased to 720° F. and maintained at this temperature for a period of ten days without any failure in the circulation of the liquid. During this operation, the lower boiling components were separated and accumulated in the storage and expansion tank, as analysis of the material in this tank demonstrated.

Numerous changes may be made in the gas separator without departing from the spirit of the invention. For example, the pipe 10 need not extend into the separation chamber 9. In this event, gaseous low-boiling substances are not collected in an upper portion of the chamber 9 but pass directly through the pipe 10 into the storage tank as they are formed. The system, nevertheless, operates under a static head of pressure equal to the pressure exerted by the liquid in the storage tank and in the pipe 10 upon the circulating liquid.

The system may also be operated with the pump located in the line 20 between the generator and the load unit. In this embodiment the gas separator is also located on the inlet side of the pump, that is, between the generator and the pump, and similarly connected to the storage and expansion tank by means of the vent pipe 10. Inasmuch as the liquid leaving the generator has a higher temperature than it has when returning, there will be more tendency for vapor to form. In view of the fact that the highest temperature and the point of lowest pressure is in the system at the inlet side of the pump in line 20, any vapor which can form will be generated at this point. Thus more lower boiling constituents will be removed if the pump and gas separator are located in the line 20 than if they are located in the lines 21—22 as illustrated.

In the case of tetra-aryl orthosilicates, it is desirable to remove the smallest amount of phenol and other decomposition products possible and still maintain circulation, as explained heretofore. For this reason, in a system using the aryl orthosilicates as a heat transfer medium, it is highly desirable to locate the pump and gas separator in the return line as illustrated. In the case of other heat transfer liquids, such as, for instance, hydrocarbon oils, where there are no reversible reactions and where the removal of larger amounts of low boiling components does not affect the system, it would be just as advantageous to locate the pump and gas separator in the line 20 provided, of course, the gas separator is adjacent the inlet side of the pump.

Although application of the invention to heat transfer liquids composed of tetra-aryl orthosilicates and hydrocarbon oils has been described, obviously the invention is useful with heat-decomposable heat transfer liquids of all types, including mixtures of other silicate esters and also nonsilicates, such as aroclors (chlorinated diphenyls), and other liquids which liberate low-boiling components when maintained at a high temperature over long periods of time.

Since many other changes and modifications will be apparent to those skilled in the art, it is to be understood that the invention is to be limited only by the scope of the appended claims.

We claim:

1. A heat transfer system for use with heat transfer liquids of the type which liberate low-boiling substances which comprises in combination, storage means for receiving liquid from and returning liquid to the system, and in sequence as named, means for heating the liquid, means for conveying liquid to a load to be heated, a load unit to be heated, means for reconveying the liquid comprising means for separating gas from said liquid which comprises a separating chamber, constructed for receiving gaseous low-boiling substances in an upper part thereof and means for discharge of gas therefrom, comprising a pipe extending downwardly into said chamber through said gas receiving portion thereof the lower end of which pipe is normally immersed in liquid disposed in said chamber, whereby discharge of gas therethrough is regulated by the pressure of gas in said receiving means, discharge of gas being permitted when said gas has attained a pressure which depresses the liquid level below the lower end of said pipe and is prevented when it has not attained a pressure sufficient to depress the liquid level below the lower end of the pipe, and means for circulating liquid.

2. A heat transfer system for use with heat transfer liquids of the type which liberate low-boiling substances which comprises means for heating the liquid, means for conveying liquid to a load to be heated, means for reconveying the liquid to the heating means, storage means for receiving liquid from and returning liquid to the system, liquid circulating means for circulating liquid through said system, and gas separating means for removing gas from said liquid including a chamber adapted to receive gas in the upper portion thereof and having means for the discharge of gas from said upper portion to said storage means, said gas separating means being located between the load to be heated and the circulating means.

3. A process of transferring heat with a heated disassociated liquid, comprising a silico-organic compound having the formula $Si(OR)_4$ in which R is selected from the group consisting of alkyl and aryl groups which comprises heating said liquid, circulating the liquid to the material to be heated, separating components boiling lower than the temperature of the liquid at the point of lowest pressure in the system, condensing at

least part of said lower-boiling components in a separate chamber and maintaining said condensed lower-boiling substances separated from, but in contact with, the circulating liquid.

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