

ALIEN PROPERTY CUSTODIAN

COOLING AND HEATING LIQUIDS

Ludwig Beer, Herbert Berg, and Wolfgang Gruber, Burghausen, Germany; vested in the Alien Property Custodian

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The art presents plenty of examples in which the applying of cooling or heating liquids, resp. of liquids causing alternatively cooling or heating would be naturally desired. As for regulations of the temperature which are to act much above 100° the real applying of cooling or heating liquids is relatively seldom; the reason for this lies in the fact that a heating and cooling liquid, favorably to be applied in general, ought to have a great selection of properties, which none of the liquids hitherto taken into consideration possesses: Such a liquid ought to be cheap and unchangeable in continuous operations, it ought to have a high boiling point in order to avoid pressure apparatus, in spite of this, however, it ought to be stable in such a degree that—even at temperatures above 200°—it does not separate incrustations on the cooling or heating surfaces nor should it corrode the surfaces. A great difficulty is added by the fact that usually metallic especially iron surfaces are applied which have a catalytic decomposing effect on most of the high boiling organic substances. Further, in spite of its high boiling point, such a liquid ought to be fluid, possibly thin fluid at usual temperatures. If the cooling or heating requires that the liquid is pumped in circulation, a new requirement is added: the liquid must not destroy lutings, stuffing boxes and the like by unrolling resp. by degreasing them.

None of the high boiling liquids hitherto taken into consideration complies with these conditions: e. g. diphenyl proposed for the heating of baking ovens is too much expensive as to be generally applied, beside this it freezes at 70.5°. High boiling oils of the type of tricresylphosphate, of the phthalic acid esters and the like are also too expensive and decompose themselves surprisingly quickly in iron vessels already at temperatures between 150-200°, whereby the heat transferring surfaces become incrustated. Glycerol decomposes itself still more rapidly. Also oils of the type of the superheated steam cylinder oils—alluring naturally by their cheapness—resinify too rapidly. Moreover their large viscosity at usual temperature is a great disadvantage.

Now it has been found that isophoron, which may be obtained very cheaply from the residues of distillation of the manufacture of acetone, comprises in itself all properties desirable for a cooling or heating liquid as described above, exceptional its capacity of dissolving oils which is also common to diphenyl, phthalic acid esters, glycerol and the like. For a great number of applications it represents an ideal heating and cooling liquid.

It is here the question of a completely new suitability opposite to all expectations, because isophoron was expected to incline to decomposition under the conditions taken here into con-

sideration and because this substance resinifies rapidly indeed if being heated in the air. The required exclusion of air, however, may be easily realized in practice.

5 Still more surprising is the further finding that isophoron prevents the decomposition of liquids inclining naturally to decompose at high temperatures if it is added to them. Therefore it is possible at first to apply easily the still cheaper high boiling fraction of the last runnings of the distillation of acetone, e. g. acetone oil boiling between 161 and 187° or between 188 and 211° instead of isolated isophoron. Moreover the possibility is given to add oils properly useless but capable to raise the boiling point, especially those as e. g. the cheap superheated steam cylinder oils which have a lubricating effect on packings and stuffing boxes. By these lubricating oils, made useful by the combination with isophoron according to the invention, it has been possible for the first time—in spite of the natural capability of the isophoron to dissolve oils—to move high boiling cooling and heating liquids in circulation for continuous operations with the aid of pumps. Thus there has been found a method for solving of the difficulties in those cases, when large quantities of heat must be led off or added through relatively small wall surfaces.

Various proposals for apparatus in which heating and cooling liquids may be used have already been made. E. g. a heat exchanger may be mentioned for carrying out exothermal catalytic gas reactions, provided with numerous thin walled tubes vertically arranged for receiving the granulous or powdery contact substance, and with two tube bottoms tightening the ends of the tubes, whereby a middle room provided with two openings—one for leading off and one for adding a refrigerant—is separated from two receivers provided with two openings, one for leading off and one for adding reaction gases. But all these proposals were practically useless if the heat exchange had to be carried out at temperatures above 100°. Only by finding liquids containing isophoron the method of heat exchange can be really applied also in these cases. Hereby superheated zones in the catalyst—causing secondary reactions and soon deteriorating of the catalyst—are avoided. Therefore it is no longer necessary to keep the temperature below the optimum in those parts of the reaction room, entered first by the reaction components, a method known for reducing the capacity of the whole reaction room. By equally regulating the temperature also the great passing through of the reaction components—formerly necessary for avoiding local superheating and thereby reducing the concentration of the reaction products—can be much diminished. By avoiding both disadvantages it is possible to make accessory apparatus much more

compendious, e. g. evaporators, preheaters, condensers for reaction products, circulation pumps. At the same time the required expense of heat is importantly reduced.

The way of applying cooling or heating liquids containing isophoron, resp. the equipment of the apparatus to be applied for the heat exchange, depends naturally on the thermal and chemical conditions in each case. E. g. if producing thermally vinyl acetate in the above described tube oven, it has been proved to be useful that the diameter of tubes for the catalysts may not be wider than 50 mm. It has been found that the catalysts can be brought in very comfortably even if the tubes are narrower than 50 mm and that the filling is much more uniform than it would be in wide one tube ovens. The discharging of the used up catalyst from the narrow tubes can also be easily carried out e. g. with the aid of hot water or vapors whereby even no dust is formed. One of the numerous possibilities of applying the new liquids may be illustrated by the following description of producing vinyl acetate:

Example

The well known catalyst, consisting of active carbon, impregnated with zinc acetate was filled into the tubes of a tube oven according to the above mentioned heat exchanger, which was provided with 51 tubes of 35 mm diameter in the clear, of a length of 155 cm and of a capacity of 76 liters; the oil container, provided with inlet and outlet tubes for the cooling and heating liquid, contained about 90 liters. The oil circulated through the apparatus, whereby a pump, a heater and a condenser were used. After removing the air by nitrogen the whole oil system was filled up with a mixture of one part of acetone oil of the boiling point of 188–211° and two parts of superheated steam cylinder oil. In order to condensate the acetone oil which evaporizes at the higher end temperatures, a condenser filled up with nitrogen, was connected with the oil container. Slight boiling did not occur before 210°.

At the beginning of the oil circulation the oil was heated at first up to 160°. Then a mixture of acetylene and vapors of acetic acid, heated in a preheater up to 155°, was blown through the catalyst tubes in such a way, that the mixture entered the apparatus at the bottom and left it at the top. The leaving mixture of gas vapors was freed from the produced vinyl acetate and the abundant acetic acid by a condenser. The acetylene not used up was led back into the process by circulation together with some fresh acetylene after having removed some waste gas. With an acetylene circulation of 7 cbm pro hour and a passing through of 8.2 kg of acetic acid pro hour (relation of acetylene to acetic acid = 100:50, time of stay in the oven 25 sec.) the condensed raw reaction product contained 50% of vinyl acetate. With an acetylene circulation of 7 cbm pro hour and a passing through of only 5.7 kg of acetic acid pro hour (relation 100:35, time of stay in the oven 28.8 sec.) a raw product containing 80–90% of vinyl acetate was obtained. With an acetylene circulation of 8.1 cbm pro hour and a passing through of 5.7 kg of acetic acid pro hour (relation 100:30, time of stay 25.8 sec.) the obtained vinyl acetate concentration was 96%. After 1310 hours the catalyst was not used up. During this time the temperature of

the cooling liquid was gradually increased up to 212°. Correspondingly a complete equally proceeding increase of the temperature up to 213–215° occurred in the reaction tubes. The average production was 1,6 kg of vinyl acetate pro liter of catalyst room and pro day. If working in order to get specially high capacities—which can be attained by giving up an extremely high concentration of vinyl acetate and also by a somewhat quicker increase of the reaction temperature—productions until 2 kg of vinyl acetate pro day and liter can be obtained.

The effect of the regulation of the temperature according to the invention is shown by an extremely equal regulation of the particularly desired temperature in the whole catalyst room. The result is—beside the increase of the output and the concentration—a complete decline of by-products like acetone and ethylen diacetate which otherwise are obtained, and a large decrease of decomposition gases. The obtained vinyl acetate is very much inclined for polymerizing and is especially pure. For instance in the block-polymerization the undesired red color of the polymers does not occur. Eliminating the by-reactions, the life time of the catalyst is naturally prolonged. The packings and stuffing boxes are permanently automatically relubricated. In this process the oven for the reaction and all accessories are much more compendious than those in the method of working hitherto applied.

For comparison: a one tube oven yielded, under the same working conditions but without the described regulation of temperature by oil, only an output of 0,9–1 kg of vinyl acetate pro day and liter catalyst room—the concentrations of vinyl acetate lying between 12–18%—though the passing through was fourfold larger and the relation of acetylene and acetic acid was 100:20. Thereby the obtained vinyl acetate contained already remarkable amounts of acetone and other impurities. Working in this way it is of course also possible to increase the concentration of the produced vinyl acetate by diminishing the passing through and increasing the reaction temperatures, but thereby the output is reduced and the impurities increase importantly.

The application of the new cooling and heating liquids, described above in a special example, can be made suitable in a wide extent for the conditions of other cases and thereby it can be usefully applied for the most different kinds of heating and cooling. E.g. in contrast to the above described method of producing vinyl acetate the cooling liquid may be formed in such a way, that the reaction heat is led off partly or for the most part as evaporation heat into a condenser by using an isophorone, mixed with much lower boiling constituents as cooling liquid. E.g. an acetone oil of the boiling point of 161–187° still contains sufficient isophoron to grant the required stability of the whole liquid mixture.

By usefully applying liquids containing isophoron also the following thermal processes can be improved: e.g. the production of vinyl chloride, of vinyl acetylene, of acrylic acid nitril and the like, condensation reactions as for instance the well known condensation of diamines with dicarbonic acids, polymerizations carried out continuously in tube shaped systems, and the like.

LUDWIG BEER.
HERBERT BERG.
WOLFGANG GRUBER.