

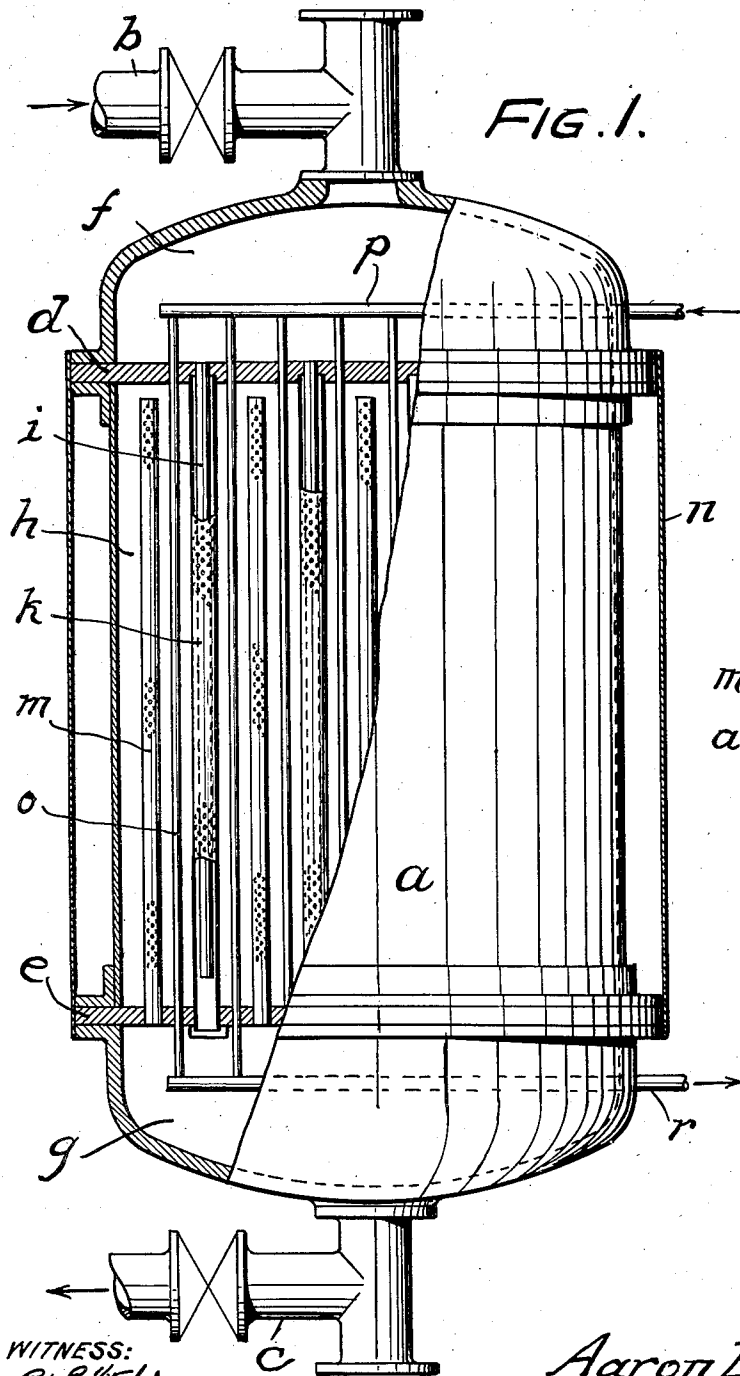
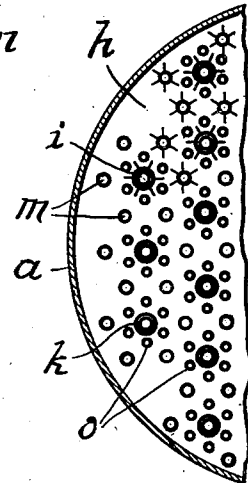
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A. B. BAGSAR

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APPARATUS FOR TREATING HYDROCARBON OILS

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INVENTOR

Aaron B. Bagsar
BY
Bussier and Harding
ATTORNEYS.

UNITED STATES PATENT OFFICE

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APPARATUS FOR TREATING HYDROCARBON OILS

Aaron B. Bagsar, Lansdowne, Pa., assignor to Sun Oil Company, Philadelphia, Pa., a corporation of New Jersey

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6 Claims. (Cl. 196—133)

In apparatus for catalytically transforming, decomposing, converting, or otherwise treating, hydrocarbon oils, as, for example, by passing hot higher boiling petroleum fractions in vapor phase through a chamber containing a catalyst followed by passing regenerating fluid through the catalytic chamber to effect removal of combustible materials, it is important to control the temperature. The desired temperature is usually approximated by pre-heating the hydrocarbon vapors and regenerating gases. In some procedures the net reaction is endothermic and in others exothermic and it is therefore often necessary, and always advantageous, to supply or abstract heat from the catalytic chamber to compensate for the heat lost or gained by the endothermic or exothermic reaction. It is known to accomplish this by flowing a heat exchange fluid through the mass of contact material in direct heat relation, but out of contact, with the catalyst. The most effective heat exchange media for thus maintaining practically constant the temperature during the said on-stream and off-stream cycle are mixtures or solutions of salts, of different composition, which are liquid at the temperature at which they enter the catalytic chamber. As examples of efficient salt compositions may cited:

KNO_3 , 45–60%; NaNO_2 , 55–40%

KNO_3 , 50–56%; NaNO_2 15–44%; NaNO_3 , 0–35%

KNO_3 , 50%; NaNO_3 , 20%; $\text{Ca}(\text{NO}_3)_2$, 30%

KNO_3 , 35%; NaNO_3 , 20%; $\text{Ca}(\text{NO}_3)_2$, 45%

The most effective way of utilizing such salts is to flow them through a multitude of small diameter tubes, which may or may not be provided with fins, extending preferably vertically through the bed of contact material, although other arrangements are known. Such tubes have usually been made of straight low carbon steel containing the usual percentage of manganese, but these are susceptible to rather rapid corrosion by the salts, which necessitates frequent replacement. Such corrosion increases with extreme rapidity through a range of temperatures from about 350° F. to 1050–1100° F. Then, too, carbon steel absorbs nitrogen from the hot salts, forming either a solid solution of nitrogen in iron, or iron nitride needles, depending on the amount of nitrogen absorbed and on the thermal cycle that the steel

tube is subjected to, with resultant increase in hardness, and corresponding decrease in ductility, of the metal. This absorption of nitrogen is very pronounced, even after relatively short exposures, at temperatures approaching 1050–1100° F. Another objection to plain carbon steel is that it becomes embrittled by prolonged exposure to the salts at temperatures above about 950° F.

That various high alloy steels, especially those having a high percentage of chromium or of chromium and nickel, offer pronounced resistance to certain types of corrosion is known, but such high alloy steels are open to certain serious objections. Their thermal conductivity is distinctly inferior to that of ordinary steel. Their high thermal expansion is objectionable, in that if the tubular elements are made therefrom it may be necessary to make the entire equipment of the same composition. They are not readily weldable under field conditions and they require some heat treatment after welding. Finally, such tubes are too expensive to justify their use for the purpose of eliminating the defects of plain carbon steel, even if it were possible to discover any such high alloy steel that would not be open to the objections specified.

Therefore, the practical commercial problem, which it is the object of my invention to solve, is to produce an alloy steel which will have a high resistance to corrosion by the particular salts that are used as heat exchange media in processes for catalytically treating hydrocarbon oils, which will have a much less tendency to absorb nitrogen from the hot salts, which will not become seriously embrittled by prolonged exposure to the hot salts, which is substantially as workable and weldable as plain carbon steel, and the cost of which does not greatly exceed that of plain carbon steel.

For several years, under my supervision, many low alloy steels have been subjected to various and exhaustive tests to determine the possibility of meeting the particular combination of requirements above mentioned. As a result of such tests I have found it possible to produce a steel alloy that meets the above requirements. The total percentage of the alloying ingredients, other than carbon and the usual percentage of manganese and silicon, need not exceed one per cent., although a substantially higher, but still low, per-

centage is preferred. The different compositions that I have found to meet said requirements come within the ranges set forth in the column below entitled "permissible range," those which meet such requirements most satisfactorily are within the column entitled "preferred ranges"; and typical compositions are in the columns so entitled. The percentage of iron is not specified, since the balance is substantially all iron.

	Permissible ranges	Preferred ranges	Typical compositions	
Carbon	<.50%	<.20%	.12%	.15
Manganese	.25-2.0	.30-.75	.50	.40
Silicon	.10-2.5	.15-1.50	.75	1.25
Chromium	.0-3.0	.50-1.25	.75	.50
Nickel	.70-5.0	1.50-3.50	3.00	2.00
Molybdenum	<3.0	.25-1.00	.75	.25
Copper	.0-2.0			
Total Cr, Ni, Mo and Cu	.70-13.0	2.25-5.75	4.50	2.75

In the preferred and most efficient compositions, the percentage of Ni substantially exceeds that of any other alloying element, also exceeds the percentage of chromium plus molybdenum and is not substantially less than, and may exceed, the percentage of chromium plus molybdenum plus either manganese or silicon. A small percentage of molybdenum must be included where strength at high temperature and insusceptibility to embrittlement are desired.

The percentages of the various ingredients may be varied within the ranges above specified dependent upon the relative importance, in the particular catalytic apparatus and the process practiced therein, of resistance to corrosion by the heat-exchange salts, resistance to nitrogen absorption, resistance to embrittlement, the necessity for ready workability and easy welding, and the factor of expense of the alloy steel. Therefore it cannot be said that any specific composition within the distinctly preferred range is superior to any other specific composition within such range.

Any composition with the wider range set forth in the above table has a corrosion rate much less than that of carbon steel. Most of such compositions and (it is believed) all of them within the preferred range have a corrosion rate from one-fifth to one-half that of plain carbon steel when exposed to said salt mixtures at high temperature. Moreover the rate at which corrosion increases with increase of temperature (say from 850° F. to 1050-1100° F.) is very much higher with plain carbon steel than with alloy steel of the composition described.

In catalytic processes in which hydrocarbons are treated as hereinbefore explained, a very efficient construction is that illustrated in the accompanying drawing, in which Fig. 1 is a vertical sectional view through the catalytic chamber and Fig. 2 a partial cross-section through the same.

The illustrated apparatus, which is substantially like that disclosed in the Pew Patent No. 2,248,118, issued July 8, 1941, comprises a cylindrical casing *a* having an oil vapor inlet *b* and an oil vapor outlet *c*. Tube sheets *d* and *e* provide top and bottom headers or manifolding chambers *f* and *g*, and between them the reaction zone or catalytic treating chamber *h*, which is substantially filled (except for the space occupied by the tubes hereinafter described) with any suitable siliceous or adsorptive catalyst which may be found effective for the reaction described. A multiplicity of tubes *k* extend between the tube sheets. Within the tubes *k* extend vapor inlet tubes *i*. The tubes *i* open at the bottom into the space enclosed by the tubes *k* and open at the top into the upper header *f*. The tubes *k* are

closed at the bottom and also at the top except to allow the extension through the tube sheet *d* of the upper ends of the tubes *i*. A multitude of vapor outlet tubes *m* are carried by and extend through the lower tube sheet *e* and there communicate with the lower header *g*. Tubes *m* extend upward through nearly the entire height of the chamber and are closed at the top. Tubes *k* and *m* have perforated walls. Each tube *k* has spaced from it, at short distances and in symmetrical relation, a number of tubes *m*. Oil vapors flowing from inlet *b* pass through the upper header *f* and tubes *i* into tubes *k*, thence laterally through the perforations in tubes *k*, thence through the catalytic material with which the chamber is packed, thence through the perforations in tubes *m* into such tubes, and thence through such tubes into the lower header *g* and out through the outlet *c*.

The casing *a* should be insulated from the surrounding atmosphere by any suitable means such as a jacket *n* for hot gases or insulating material.

The tubes hereinbefore described whereby the mixtures or solutions of salts flow in heat exchange relation with the catalyst are marked *o* in the drawing. These tubes, which are of course imperforate, are preferably more numerous than the oil inlet and outlet tubes and extend vertically entirely through the catalytic chamber and through both tube sheets into the headers *f* and *g*. The tubes *o* communicate at opposite ends with tubes *p* and *r* for supplying the salt mixture to and removing it from the tubes *o*. The tubes *o* are symmetrically arranged relatively to each other and to the tubes *k* and *m*.

As before stated, the hot oil vapors in the on-stream part of the cycle, and the regenerating medium in the off-stream part of the cycle, pass through the contact bed from one set of tubes *k* to the other set *m*, while the salt mixtures continuously flow through the tubes *o*. The temperature of the salts flowing through tubes *o* is such as to supply or abstract heat from the catalytic chamber to compensate for the heat lost or gained by the endothermic or exothermic reaction and their distribution is such as not only to maintain the catalytic mass at a predetermined, usually constant temperature, but also so to maintain such temperature substantially uniform throughout the entire catalytic mass.

While the salt mixtures are not in direct contact with any tubes except those through which they flow, the other tubes are indirectly affected by any corrosion or embrittlement of, or nitrogen-absorption by, the salt tubes, and it is therefore highly desirable to make these fluid inlet and outlet tubes of the same material as the salt carrying tubes. The inlet and outlet tubes for inflow and outflow of oil vapors and regenerating media are also, in such catalytic apparatus, provided with fins, which are welded thereto, ready weldability of the alloy steel being hence of great importance.

It is also of advantage, for other reasons, to make the said oil inlet and outlet tubes of the described composition, since such tubes of such composition are well adapted to resist corrosion due to the hydrogen sulfide, produced by conversion thereto of the sulfur in the hydrocarbon oil, which attacks and corrodes plain carbon steel. It is known that resistance to such corrosion may be materially increased by making the tubes of a low carbon steel containing, in addition to a percentage of manganese within the usual range in carbon steel, a percentage of chromium not less

than four per cent to which is usually added about one half of one per cent. of molybdenum. I have discovered that the efficiency of tubes of the described composition to resist corrosion is materially lessened when, as is usually or frequently the case, an appreciable percentage of salt is present in the oil, since chromium steels are more liable than carbon steels to corrosion by chlorides. While the composition herein described is more particularly intended and adapted for use in the manufacture of the heat-exchange salt solution tubes, it has been found that, probably due mainly to their nickel content and their low chromium content, they have the effect of imparting to the inlet and outlet tubes a substantially greater resistance to corrosion by salt than the high chromium tubes with no diminution in their resistance to corrosion by hydrogen sulfide.

In an application filed by me August 28, 1940, Serial No. 354,584 and also in an application, Serial No. 453,713, filed August 5, 1942, as a continuation in part of Serial No. 354,584, I have described catalytic oil conversion apparatus made of alloy steels within the ranges herein described, comprising oil inlet and outlet tubes but not necessarily also comprising heat-exchanging salt-carrying tubes. Where protection from corrosion of the oil inlet and outlet tubes (receiving oil containing sulfur and salt impurities) is the primary consideration, it is highly desirable that compositions within the ranges herein specified shall have a silicon content substantially in excess of the chromium content and not less than half the nickel content, as in one of the two typical compositions herein set forth. Since the last named specific composition is not of pronounced advantage over other compositions within the ranges claimed herein for use in the manufacture of heat-exchanging salt-carrying tubes, I have not herein claimed oil inlet and outlet tubes of such specific composition but have made them the subject-matter of the claims in said application Serial No. 453,713.

My invention does not depend for its novelty upon the novelty of the composition per se, my discovery being the adaptability of the composition to the manufacture of the tubular elements, particularly but not exclusively to the salt-carrying heat exchange tubes, in apparatus for the catalytic treatment of hydrocarbon oil, for the purpose and with the result of accomplishing the objects hereinbefore explained.

In claiming iron as constituting substantially all the balance of the composition, I do not exclude the addition, in very small proportions, of other elements whose addition would not unfavorably affect the function of the combination of elements particularly recited. Among such elements one or possibly more of which may be added in very small proportion, are aluminum (which may in part replace the silicon) and elements like columbium, tantalum, titanium and vanadium which are commonly added to chromium steel and chromium-nickel steel but whose addition, in my composition, is unnecessary (even though sometimes advisable) due to the small chromium content.

What I claim and desire to protect by Letters Patent is:

1. An apparatus for use in processes for conversion of hydrocarbon oils at high temperature

in the presence of a catalyst, said apparatus comprising tubes extending through the catalyst and adapted to carry salts to extract heat from or supply heat to the catalytic material and being composed of an alloy steel resistive to corrosion, embrittlement and absorption of nitrogen, said alloy containing carbon less than .5%, manganese .25 to 2.5%, silicon .10 to 2.5%, chromium not to exceed 3%, nickel .70 to 5%, and molybdenum .25 to 3%, the balance being substantially all iron.

2. An apparatus for use in processes for treating hydrocarbon oils at high temperature in the presence of a catalyst, said apparatus comprising inlet and outlet tubes through which oil and regenerating fluid are supplied to and removed from the catalyst and heat exchange tubes extending through the catalyst and adapted to carry salts for extraction of heat from or supply of heat to the catalytic material, said tubes being composed of the alloy defined in claim 1.

3. An apparatus for use in processes for conversion of hydrocarbon oils at high temperature in the presence of a catalyst, said apparatus comprising tubes extending through the catalyst and adapted to carry salts to extract heat from or supply heat to the catalytic material and being composed of an alloy steel resistive to corrosion, embrittlement and absorption of nitrogen, said alloy containing carbon less than .2%, silicon .15 to 1.5%, manganese .3 to .75%, chromium .5 to 1.25%, nickel 1.5 to 3.5%, and molybdenum .25 to 1.0%, the percentage of nickel exceeding that of any of the other alloying elements, the balance being substantially iron.

4. An apparatus for use in processes for treating hydrocarbon oils at high temperature in the presence of a catalyst, said apparatus comprising inlet and outlet tubes through which oil and regenerating fluid are supplied to and removed from the catalyst and heat exchange tubes extending through the catalyst and adapted to carry salts for extraction of heat from or supply of heat to the catalytic material, said tubes being composed of the alloy defined in claim 3.

5. An apparatus for use in processes for conversion of hydrocarbon oils at high temperature in the presence of a catalyst, said apparatus comprising tubes extending through the catalyst and adapted to carry salts to extract heat from or supply heat to the catalytic material and being composed of an alloy steel resistive to corrosion, embrittlement and absorption of nitrogen, said alloy containing carbon less than .2%, silicon .15 to 1.5%, manganese .3 to .75%, chromium .5 to 1.25%, nickel 1.5 to 3.5%, and molybdenum over .25 but less than 3%, the total percentage of nickel, chromium and molybdenum not exceeding 6% and the percentage of nickel exceeding that of any of the other specified alloying elements.

6. An apparatus for use in processes for treating hydrocarbon oils at high temperature in the presence of a catalyst, said apparatus comprising inlet and outlet tubes through which oil and regenerating fluid are supplied to and removed from the catalyst and heat exchange tubes extending through the catalyst and adapted to carry salts for extraction of heat from or supply of heat to the catalytic material, said tubes being composed of the alloy defined in claim 5.

AARON B. BAGSAR.