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APPARATUS FOR CRACKING HYDROCARBON OILS

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This invention relates generally to apparatus for decomposing or converting hydrocarbon oils, as, for example, the subjection of higher boiling petroleum fractions to a high temperature to effect their partial conversion to lower boiling hydrocarbons. Such conversion is commonly effected by a purely thermal process in tubular coil stills and is also effected catalytically, at lower, but still high, temperatures, in catalytic case tubes. As is well known, when such stills are composed of ordinary carbon steel, the sulfur contained in the oil is converted to hydrogen sulfide and other sulfur compounds, which attack and corrode the steel and materially shorten the life of the still. It is known, however, that resistance to corrosion may be materially increased by making the stills, or the tubular elements thereof, of a low carbon alloy steel containing, in addition to a percentage of manganese within the usual range of carbon steel, a percentage of chromium not less than 4%, to which is usually added about .5% of molybdenum. A typical commercial composition is: C .12%, Mn .31%, Cr 4.6% and Mo .50%.

I have discovered that the reliability and efficiency of stills for decomposing hydrocarbon oils at high temperature made of alloy steel of a composition similar to that specified 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 steel to corrosion by chlorides. I have also discovered that, in commercial chromium steels of the order of that above specified, it is possible to largely replace the chromium by nickel and thereby materially decrease the corrosion due to the presence of salt without diminishing resistance to corrosion due to sulfur. I have also discovered that resistance to corrosion is still further increased by utilizing a percentage of silicon greater than that usually present in carbon steel, the silicon securing increased resistance to sulfur and salt corrosion on the inner surface of the tubes exposed to sulfur-containing hydrocarbons and increased resistance to sulfur corrosion and oxidation on the outer surface of the tube produced by combustion products of the fuel. Molybdenum is known to increase the strength of the alloy at high temperature and for reducing susceptibility to embrittlement. It is also possible to replace the silicon in part with aluminum, which performs essentially the same function as silicon except that it does not substantially reduce salt corrosion, and which I have found, even when added in a much smaller percentage than one per cent., reduces scaling and oxidation of the steel to a far greater extent than silicon alone. In some service conditions, however, aluminum-bearing chromium steel, even when containing molybdenum, is susceptible to embrittlement and it is therefore desirable to add a substantially smaller percentage of aluminum, preferably less than 1%, than would be desirable if resistance to oxidation were the only factor to be considered; in other words, to add aluminum, if added at all, only when molybdenum is added in sufficient proportion to counteract the embrittling tendency of the aluminum. It is also desirable, but not necessary, to add titanium, which, besides increasing the tendency to scaling, reduces the air-hardening tendency of the steel especially if the steel contains over one per cent. of chromium. It is also desirable, but not necessary, to add vanadium, and thereby obtain other desirable properties, including carbide stabilization and structural uniformity.

The following composition is found to be measurably superior in corrosion resistance to the commercial chromium-molybdenum steel hereinbefore mentioned:

C .14%, Mn .44%, Cr .8%,
Ni 1.5%, Si 1.2%, Mo .5%

It will be observed that in this composition the percentage of each of the elements Ni and Si is substantially higher than the percentage of Cr, that the percentage of Si is not much lower than that of the Ni, and that the combined percentage of alloying elements, other than C and Mn, is only 4%.

The following are other example compositions that are highly resistant to corrosion:

	II	III	IV	V	VI	VII
C	.09	.08	.1	.1	.08	.2
Mn	.38	.29	.3	.4	.6	.6
Cr	.9	.7	.5	.2	1.8	1.2
Ni	1.2	.9	2.0	2.4	3.5	2.5
Mo	.4	.7	.4	.4	.2	.7
Si	1.5	.8	1.0	1.2	2.0	.8
Al		.7				.7
Ti				.3		
Va					.08	

In general, the smaller the percentage of carbon the better. A carbon percentage of .25 is about the permissive maximum. Its percentage should not exceed about .2 and is preferably considerably lower. A carbon percentage as low as .06% is commercially practicable. The only objection to steel containing very little or no carbon is the expense of its production.

The permissive ranges of alloying elements other than carbon are:

Cr less than 2%, preferably not over 1.5% and desirably a fraction of 1%, and below the percentage of nickel and below the percentage of silicon if aluminum is not added and below the percentage of silicon and aluminum if both be added, and preferably below the percentage of silicon even if aluminum be added.

Manganese .2 to 1%.

Silicon .6 to 2.5%, but preferably between .6 or .7% and 1.5 or 1.6%, and preferably above the percentage of chromium, and always together with aluminum, if aluminum be added, above the percentage of chromium. The percentage of silicon, or of silicon and aluminum if the latter be added, should not be less than half, and may exceed, the percentage of nickel.

Ni .8 to 3.5% and above the percentage of Cr.

Mo .2 to 2%; a percentage near the bottom of this range, usually .4 to 1.0%, being all that is required to give the desired strength at high temperature and to reduce susceptibility to embrittlement, a higher percentage being permissive, but necessary only if aluminum be added to replace in part the silicon.

Aluminum, if added, .1 to 1.5%.

Titanium, if added, .2 to .6%.

Vanadium, if added, .05 to .3%.

The narrow preferential ranges above specified give the highest degree of resistance to corrosion and oxidation when the oil contains an appreciable percentage of salts, although deviations therefrom within the wider ranges specified give a substantially higher resistance to corrosion and oxidation than in steel containing relatively high percentages of chromium and relatively low percentages of silicon, even when nickel is added in considerable proportion to largely replace the chromium. While the entire elimination of chromium is undesirable, its omission, provided the nickel, silicon, or silicon and aluminum, are included in the proportions specified, still produces a steel that has a higher resistance to corrosion, where salt is present in the oil, than known commercial steels containing a relatively hgh percentage of chromium.

My invention does not depend for its novelty upon the novelty of the composition per se, my discovery being the adaptability of the composition, not to corrosion generally, but to the corrosion of tube stills in which hydrocarbon oil, containing salt and sulfur, is subjected to the high temperature required to effect their decomposition or conversion.

In claiming iron approximately sufficient to complete the 100%, I do not mean to exclude the addition of elements not specified in the claims but described in the specification as desirable additions in the small proportion ranges stated, nor to exclude the addition of very small proportions of other elements whose addition would not unfavorably affect the function of the elements particularly recited.

This application is a continuation in part of an application filed by me August 28, 1940, Serial No. 354,584.

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

1. A still for use in a process wherein hydrocarbon oils containing impurities including both sulfur and salt are subjected to high temperature to effect their conversion or decomposition, which comprises a tubular container for such oils of an alloy steel containing carbon less than .25%, manganese in a proportion common in carbon steel, chromium .2 to less than 2%, nickel .8 to 3.5%, molybdenum .2 to 2%, a constituent of the group consisting of silicon and silicon plus aluminum .7 to 2.5%, and iron approximately sufficient to complete the 100%; the percentage of nickel being substantially in excess of the percentage of chromium and the percentage of said silicon-containing constituent being also substantially in excess of the percentage of chromium and not less than half the percentage of nickel.

2. A still for use in a process wherein hydrocarbon oils containing impurities including both sulfur and salt are subjected to high temperature to effect their conversion or decomposition, which comprises a tubular container for such oils of an alloy steel containing carbon less than .25%, manganese in a proportion common in carbon steel, chromium .2 to less than 2%, nickel .8 to 3.5%, silicon .6 to 2.4%, aluminum .1 to 1.5%, molybdenum in a proportion, varying approximately directly with the percentage of aluminum, within the range .4 to 2%, and iron approximately sufficient to complete the 100%; the percentage of nickel being substantially in excess of the percentage of chromium and the percentage of silicon plus aluminum also substantially exceeding the percentage of chromium and being not less than half the percentage of nickel.

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