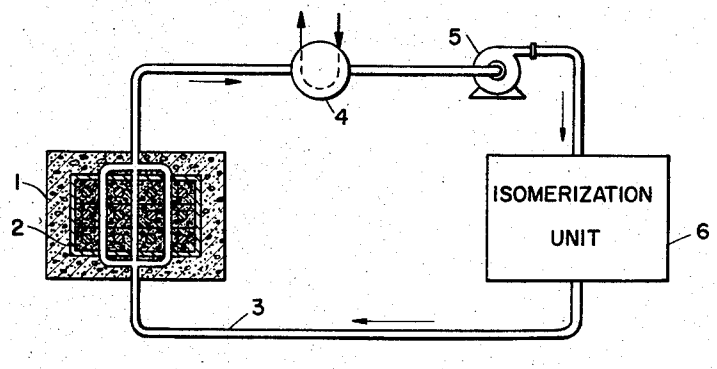
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OPERATION OF RADIATION EMITTING APPARATUS

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OPERATION OF RADIATION EMITTING APPARATUS

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This invention is concerned with the process for the operation of radiation emitting apparatus. More particularly, it is directed to the use of an operating fluid showing excellent resistance toward deteriorating influences of radiant energy.

In the operation of nuclear reactors, atomic piles, high energy electron radiation sources, Van de Graaff accelerators, linear accelerators, and the like, numerous problems arise relative to the effect of the high energy radiation upon fluids within the radiating area. These operating fluids include either liquids or gases and constitute auxiliary fuels, lubricants, greases, hydraulic fluids, coolants and moderators. The radiation combined with temperature and other effects occurring results in numerous changes in such fluids such a dehydrogenation, alkylation, polymerization, decomposition, resinification, isomerization, and free radical formation. Hence, it is a serious problem to which no fully satisfactory answer has been heretofore proposed to provide fluids which are highly resistant to radiant energy as outlined above.

Aromatic hydrocarbons have been proposed for such purposes but in many instances the stability of the aromatic hydrocarbons has been observed only when they are in essentially pure form and not mixed with paraffins or other non-aromatic hydrocarbons. It has been found that the aromatics tend to alkylate under the influence of radiation (when non-aromatics are present) and upon the formation of free radicals and within a relative short space of time the protective power of the aromatics is no longer present. Olefins in general have exhibited unsatisfactory radiation stability owing to their tendency to polymerize. Aromatic compounds not only are frequently of relatively short life in the presence of non-aromatic hydrocarbons but also are disadvantageous when used as fuel due to their smoking and burning characteristics including low heat values on a weight basis. Consequently, it is also necessary, particularly in military fuel specifications to limit the aromatic content to no more than about 20% by weight.

It is an object of the present invention to provide an improved process for the operation of radiation emitting apparatus. It is a more particular object of this invention to provide a process for the operation of such apparatus by means of a fluid showing a minimum deterioration in the presence of radiant energy. It is a special object of the present invention to provide a means for stabilizing operating fluids utilized in this general class of apparatus. Other objects will become apparent during the following discussion. Now, in accordance with the present invention, it has been found that operating fluids for radiation emitting apparatus are especially stable with respect to said radiation when they contain at least 30% by weight of cis-trans isomeric cyclic (preferably polycyclic) saturated hydrocarbons. More particularly, a process for operating radiation emitting apparatus over extended periods comprises utilizing such fluids as just described and recycling them through a converter for altering the ratio of cis and trans isomers from that which

exists at the time the fluid emerges from the radiation emitting zone.

In the operation of radiation emitting apparatus by the use of cyclic saturated hydrocarbons over an extended period an equilibrium mixture of cis and trans isomers is created. It appears that a high amount of energy is utilized in the transformation of cis to trans and in the reverse reaction of trans to cis isomer, although more energy appears to be utilized in the transformation of cis to trans. Large amounts of energy are dissipated in the absorbed ionizing energy utilized for cis-trans isomerization. Consequently, it is possible to utilize a mixture of cis-trans isomers as an operating fluid for radiation emitting apparatus which is predominant in either cis or trans isomers since the reaction proceeds in either direction to essential equilibrium under the conditions existing, said equilibrium proceeding at a rate and to an extent specific to the conditions present and the particular cis-trans isomers being utilized.

In the processes involving alteration of the balance of cis-trans isomers in a circulating process, the alteration may be effected by either isomerization or physical separation of the isomers existing, followed by recycling of all or a part of the products obtained in such processes. For example, if the cis-trans isomers possess melting points or boiling points of sufficient difference, it is possible to separate them by means of fractional crystallization or fractional distillation. Subsequently, they may be recycled to the reactor either as essentially pure cis and trans components or may be recombined in any desired ratio prior to recycling. The same is true of isomerization wherein the isomerizing process may result in a mixture of products, some of which are desirable for recycling and others of which are not. In such case, the product of the isomerizing step may be fractionated by any well-known means and a desired fraction so obtained may be recycled for use as an operating fluid in the reactor.

Still another means by which the cis and trans isomers may be segregated is by means of preferential complex formation or so-called "clathrate" formation wherein relatively unstable molecular complexes of a particular compound with a clathrate-forming material is formed and then decomposed to recover the segregated isomer which can then be recycled for use in the radiation emitting equipment

The use of cis-trans saturated polycyclic hydrocarbons for this particular purpose shows benefits when the cis-trans isomers are present to the extent of at least 30% by weight of a given fluid, although it is preferred that between about 40 and about 100% by weight of the cis-trans isomers are present. Consequently, it will be seen greases, hydraulic fluids, coolants and the like may be protected insofar as deterioration due to radiation energy by the presence of a minimum amount of about 30% by weight of the cis-trans saturated cyclic hydrocarbons.

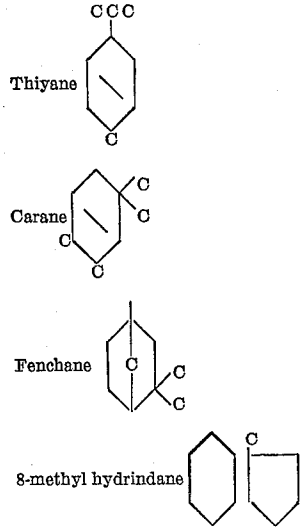
The fluids of the present invention may be utilized either in the gaseous stage or in the liquid stage or both especially when they are being utilized as coolants. In performing this function an initially liquid mixture may upon absorbing sufficient heat from a radiant energy reactor be converted to a gas or vapor and thereafter passed through a heat exchanger where it gives up its thermal energy which is then converted in mechanical energy for the operation of turbines or the like.

The saturated cyclic hydrocarbons to be employed in accordance with the present invention include those capable of forming or existing as stero isomeric pairs. Preferably those employed have boiling points in excess of about 150° C. at atmospheric pressure and still more preferably also have melting points below about 0° C. although the latter physical property is not essential for many purposes.

Table I illustrates the type of hydrocarbons which may be used but it will be understood that this list is merely illustrative to indicate the nature of the compounds and is not regarded as restricted thereto. The preferred subgeneric class of compounds to be utilized in the present processes include the bicyclic saturated hydrocarbons and more particularly, bicyclodecanes, said bicyclic hydrocarbons being either unsubstituted or bearing alkyl substituents.

Table I

[O,4,4]-bicyclodecane (Decalin)
1-methyl-[O,4,4]-bicyclodecane
2-methyl-[O,4,4]-bicyclodecane
3-methyl-[O,4,4]-bicyclodecane
1,5-dimethyl-[O,4,4]-bicyclodecane
2,8-dimethyl-[O,4,4]-bicyclodecane
1-methyl-4-ethyl-[O,4,4]-bicyclodecane
1,5-dimethyl-8-ethyl-[O,4,4]-bicyclodecane
2-ethyl-3-propyl-[O,4,4]-bicyclodecane
[O,3,4]-bicyclononane
[O,3,3]-bicyclo octane
2,2,4-trimethyl-[1,1,3]-bicycloheptane (pinane)



According to the above table, it will be seen that the bicyclo alkanes are preferred due to their optimum physical properties particularly when they contain at least about 8 carbon atoms per molecule and preferably at least about 10 carbon atoms per molecule, still more preferably between about 10 and 20 carbon atoms per molecule. The Decalins are preferred species as well as the pinanes, due to the fact that these particular materials have low melting points in the order of —30 to —50° C. and boiling points in the order of 165–193° C., depending upon the rate ratio of the cis or trans isomers present. Monocycloalkanes may be utilized if they bear 2–6 alkyl substituents and a total of at least 8 carbon atoms. Such materials include trimethylcyclohexane, diethylcyclopentane, etc.

When the above types of polycycloalkanes are utilized in conjunction with other hydrocarbons or substituents, the resulting composition should be substantially free of aromatics or olefins or at least should contain less than about 20% by weight thereof. Such compositions would be regarded as being substantially free of olefins or aromatics when the content is less than about 2% by weight thereof.

The drawing illustrates a typical process utilizing the present invention. In this figure a nuclear reactor **1** containing a radiant energy producing source **2** is cooled by means of a circulatory system **3** wherein a circulating coolant fluid passes through the reactor, absorbing heat produced by the radiant energy and is passed to the heat exchanger **4**, the fluid being moved by means of pump **5**. Either prior to or subsequent to heat exchanging, the coolant fluid is passed through an isomerization unit **6** wherein the balance of cis and trans isomers is altered

from that contained by the coolant fluid upon its egress from the nuclear reactor or radiation producing zone. After alteration of the ratio of cis to trans isomers in the isomerizer **6** the fluid is then recycled for further use as coolant in the reactor **1**.

The isomerization step per se is not regarded as a novel feature since isomerizing conditions are well known in the art of treating hydrocarbons. Consequently, it is unnecessary to present in detail the catalysts and conditions necessary for isomerization of cis-trans isomers. In general, however, isomerization is effected by the use of aluminum halide catalysts at temperatures between about room temperature and 250° C. for a period of time which may be momentary to about 4 days. The catalyst may contain promoters such as iron halide or hydrogen halides and catalysts other than aluminum chloride may be utilized, such as an alloy of nickel, cobalt and aluminum in the presence of hydrogen, or molybdenum trisulfide in the presence of hydrogen. The products of isomerization are normally an increased amount of the trans isomer with or without other isomers being formed.

While the usual nuclear reactor contains rods or other structural units of the fuel, it is possible to utilize a fluidized system wherein the mass of fissionable material of particles of fluidizable size is in heat transfer relation with the heat transfer medium which may comprise polycyclic saturated hydrocarbons such as described hereinbefore. Under these conditions, the fissionable material undergoes nuclear reaction and the energy therefrom is adsorbed by the heat transfer medium which is then conducted to an energy transfer zone and recirculated after alteration of the cis-trans balance as described herewith for further heat transfer with the fluidized mass of fissionable material. Other alterations in a typical nuclear reactor design are described by Fermi et al., U.S. 2,708,656.

The present invention may be utilized in connection with any chemical or physical reaction being conducted in the presence of radiant energy such as in the treatment of hydrocarbons or other oragnic compounds by the radiant energy obtained from radioactive by-products or a waste material of atomic piles. In such instances, the organic compounds to be treated are subjected to the radiation of spent nuclear reactive fuel elements, preferably at temperatures between about 50 and 700° F. and at radiation intensities of 50,000 to 5,000,000 roentgens per hour at pressures of 5–250 pounds per square inch absolute and at pressures of 1–50 atmospheres. The temperature range may extend to —50° F. and up to 750° F. in special instances. Atmospheres of carbon monoxide or hydrogen may be utilized or the chemical reaction may take place in the presence of oxygen. Under such treatments, paraffins and isoparaffins may be polymerized with concurrent hydrogenation while olefins and some aromatics are polymerized particularly if they are exposed in the vapor space. Alkylation reactions may be conducted under such circumstances, particularly for the alkylation of aromatics. Cracking of high molecular weight materials such as petroleum residues and waxes may be effected by such means as well.

In the conduct of such types of reactions in the presence of radiant energy, activating fluids may be necessary for the operation of moving metallic parts such as pumps, hydraulic systems and the like in addition to any cooling systems which may be necessary. It is for such purposes that the fluids of the present invention may be employed. Other reactions which take place in the presence of radiant energy include oxidation of hydrocarbons and halogenation thereof, particularly when the hydrocarbon being so treated is aromatic character.

In illustrating the stability of cis-trans saturated polycyclic hydrocarbons toward radiant energy, a mixture comprising 37.7% of trans Decalin, 57.5% of cis Decalin and 4.7% of tetralins, was subjected to radiant energy in the order of 10^8 roentgens in a spent cobalt fuel

element installation. It was found that under these conditions a final ratio of cis to trans isomer of 1.47 was obtained, only 3.9% of the product forming lower boiling materials, the product containing also 37.4% of trans Decalin and 55.6% of cis Decalin with a reduction of tetralin to 3.2%. When the resulting product is recycled to an isomerizing unit to form an increased amount of the trans Decalin it can then be recycled to further exposure to radiant energy, the absorbed ionizing energy being dissipated in transformation of the increased amount of trans Decalin so as to result in a product having a cis to trans ratio in the order of 1.47–1.50.

When a second sample of the same components is exposed, containing 33.1% of trans Decalin, 64.2% of cis Decalin and 1.7% of tetralins, the product had the following composition. After a dosage of 1×10^8 roentgens at ambient temperature, the product contained 1.2% of low boiling products, 39.3% of trans Decalin, 56.5% of cis Decalin, and 3% tetralins, the ratio of cis to trans Decalins in the exposed product being 1.44.

We claim as our invention:

1. In the operation of radiant energy-emitting equipment, wherein an operating fluid therefor is subjected to radiation, the steps comprising utilizing as the operating fluid a fluid composition comprising at least 30% by weight of cis-trans isomeric saturated cyclic hydrocarbons, any balance of the composition being other hydrocarbons, no more than 20% by weight of the composition being aromatic and olefinic hydrocarbons, subjecting said fluid to the radiation, whereby the ratio of cis-isomers to trans-isomers is increased, subjecting the mixture so formed to isomerization whereby the cis to trans ratio is substantially decreased, and recycling the resulting product for use as an operating fluid in radiation-emitting equipment.

2. In the operation of radiant energy-emitting equipment wherein heat produced by said energy is removed by a circulating coolant, heat so removed being extracted from the coolant in a heat exchanging system, the improvement comprising utilizing as said coolant a fluid comprising about 40–100% by weight of cis- and trans-isomers of saturated polycyclic hydrocarbons, any balance of the composition being other hydrocarbons, no more than 20% by weight of the composition being aromatic and olefinic hydrocarbons, said coolant being first

subjected to radiant energy, whereby the ratio of cis- to trans-isomers reaches equilibrium under the existing conditions, subjecting the irradiated coolant to isomerization whereupon the ratio of cis- to trans-isomers is substantially decreased, and recycling the coolant.

3. In the lubrication of moving metallic components of radiant energy-emitting equipment, wherein a lubricant is supplied to the lubrication sites through a circulation system and is thereby subjected to radiant energy, the improvement comprising utilizing as the lubricant a composition comprising 40–100% by weight of cis-trans isomeric saturated polycyclic hydrocarbons, any balance of the composition being other hydrocarbons, no more than 20% by weight of the composition being aromatic and olefinic hydrocarbons, the ratio of cis to trans isomers being increased upon exposure to the radiant energy, circulating the exposed lubricant through an isomerizer, wherein the ratio of cis to trans isomers is decreased, and circulating the lubricant back to the lubrication sites.

4. In the operation of a radiant-energy emitting power plant, wherein an operating fluid utilized in operation of said plant is subjected to radiation emission, the improvement comprising using as said fluid a fluid composition comprising at least 30% by weight of cis- and trans-Decalins, any balance of the composition being other hydrocarbons, no more than 20% by weight of the composition being aromatic and olefinic hydrocarbons, the ratio of cis to trans Decalin increasing during use thereof in said plant, circulating the radiation-exposed fluid to an isomerizer, wherein the ratio of cis to trans-Decalin is decreased, and then recycling the fluid in the operation of said plant.

References Cited in the file of this patent

UNITED STATES PATENTS

2,708,656 Fermi et al. ---------- May 17, 1955

OTHER REFERENCES

Proceeding of the International Conference on the Peaceful Uses of Atomic Energy held in Geneva, Aug. 8–20, 1955, vol. 7, pp. 546–555, United Nations, New York, 1956.