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Issledovaniya po primeneniyu organicheskikh teplonositeley-zamedliteley v yadernykh reaktorakh

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ANNOTATION

This paper is a review of the primary investigations of the use of high boiling organic fluids as coolants and moderators in nuclear reactors. Results of radio-chemical, thermo-physical, corrosive and neutron-physical investigations are discussed. The paper furnishes data covering the use of destructive hydrogenation for the regeneration of products of radiolysis of organic coolants.

INTRODUCTION

The specific economic and geographic peculiarities of the Soviet Union dictate the need for construction of low--cost, low power (500 - 10,000 kw) electric generating stations. Solution of this problem through the use of conventional thermal (steam and diesel) electric generating plants cannot be considered quite satisfactory, due to the high cost of the electric energy generated. This circumstance is attributable to the high fuel cost component , resulting from the high cost of fuel transportation to the remote and almost inaccessible sites of these installations. (We refer to the remote regions of the Arctic and of Siberia).

As shown by the technical-economic calculations of U.I.Koryakin and of others, employment of nuclear power plants under such conditions is found to be completely justifiable from the economic standpoint, even with their current economic characteristics.

In order to obtain the maximum economic benefit in that case, it is most important to develop a nuclear power plant having the lowest possible capital component of the cost of electrical energy generated, since in low power installations of even non-nuclear type this cost component is very high and, naturally, transition to nuclear power generation will not have the effect of lowering it. In addition, a nuclear power plant designed to operate in remote and hard to reach locations must have such characteristics as simplicity and reliability of operation, small weights and dimensions of equipment, to insure ease of transportation and so forth.

These requirements made it expedient to devote attention to nuclear power plants utilizing organic coolants--moderators, since this is one type of nuclear plant which can, more or less, satisfy the specified conditions. Established advantages of organic reactors (low pressures, low activation of the heat transfer agent, ability to utilize inexpensive structural materials and standard equipment of the "non-nuclear" type) furnished reasons to hope that their use would be expedient in this particular case.

In view of this, various laboratories of the USSR have undertaken and are currently continuing a relatively wide complex of investigations. These investigations are all related to a single plan but vary widely, both in the nature of subjects under study and in their scope (from "pure" ampoulic studies of radiolysis to the activation and trial operation of an experimental organic 300 kw reactor at the Atomic Energy Institute in 1960.

A practical embodiment of the results of these efforts was the construction and activation of the portable 750 kw "Arbus" nuclear power plant in 1963.

This paper represents an attempt to describe briefly and to draw inferences from some of the principal results of these investigations.

RADIO → - CHEMICAL STUDIES.

At present it is commonly known that the aromatic hydrocarbons possess the highest radio → - thermal stability among all of the organic compounds. However, their relatively high melting points represent a serious shortcoming. Due to the fact that the ultimate goal of our investigations, as stated above, was the development of a low-power, largely self-contained nuclear power plant, employment of pure polyphenyls as cooling agents appeared unacceptable.

Taking into account the known protective effect of the aromatic compounds in various combinations with organic components of the non-aromatic type, we decided to investigate the radio → - thermal stability of such compositions. From the standpoint of convenience and economy of operation of a nuclear power plant utilizing an organic coolant, not the amount, proper, of radio → - chemical yield of products of radiolysis per unit of energy absorbed by the coolant, but the resulting level of radiolytic losses of the coolant is of the greatest importance. This factor is determined by both the coolant's stability and by its ability to regenerate its products of radiolysis with assurance of minimum loss. In addition, naturally, the cost and availability of the various organic coolants and the nature of the products formed during their radiolysis (particularly, tendencies to precipitate as insoluble particles or films) are the important factors to be considered.

With these considerations in mind, concurrently with a series of investigations of radio → -thermal stability, we made studies of the possibility of destructive regeneration of high boiling products of radiolysis which furnished some very satisfactory results. Among a number of alkyl - generating polyphenyls, we investigated industrial monoisopropyldiphenyl and the vat residues from the production of cumene (isopropylbenzene). Experiments of U.N.Aleksenko and V.A.Khramchenkov with monoisopropyl - diphenyl were performed in the VVR-2 reactor, with exposure of specimens made at temperatures ranging from room temperature to 380° C in ampoules, also in loop installations at temperatures approximating 200° C (temperature at the surface of the fuel elements in this experiment was approximately 320 - 350° C). In this experiment we used an industrial plant product containing approximately 15 % of unalkylated diphenyl and approximately 5 % of the heavier products (principally - diisopropyldiphenyl).

This product has the following characteristics:

Melting temperature	- 40° C
Boiling temperature	270-290° C
Molecular weight	196
Ratio of carbon to hydrogen contents (atomic)	0.95

Preliminary investigations of thermal stability of monoisopropyldiphenyl in an industrial nitrogen atmosphere[1] have shown that the pyrolytic process of this substance progresses quite sluggishly up to 360° C and that it is accompanied by the formation of a small amount of high boiling product and a weak emission of gas. The rate of formation of high boiling products within this temperature range is approximately constant with time and increases slightly with the temperature.

Within the temperature range of 360-420° C the process does not change qualitatively, but there is a noticeable tendency toward an exponential increase in the rate of formation of high boiling products with time and the energy of activation increases appreciably. Finally, at 420° C there is a qualitative change in the process, characterised by the start of violent liberation of gas, abrupt increase in

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[1] U.N.Aleksenko, V.A.Khramchenkov. Thermal stability of monoisopropyldiphenyl. Atomic Energy, Vol. 13, First Edition, p. 47 (1962).

the rate of formation of high boiling products and precipitation of insoluble coke - like particles, this is , apparently, the start of an intensive pyrolytic cracking process of monoisopropyldiphenyl. The high boiling product formed during pyrolysis has an average molecular weight of 265, which is approximately a 1.5 - fold increase, compared to the molecular weight of the original substance.

Figure I shows the curves representing the accumulation of high boiling products of monoisopropyldiphenyl, for various dosages of exposure. A typical characteristic of these results is the absence of retardation of formation of high boiling products as they accumulate. These results also confirm the existance of a range of temperatures (approximately 200-350° C) in which the rate of formation of high boiling products is slower. On the basis of this data, Figure 2 shows the relation of the radio-chemical liberation of high boiling products in monoisopropyldiphenyl to the temperature of radiolysis (in this case, and from here on, the calculation of radio-chemical liberation of high boiling products is made for the number of molecules of the original substance transformed into high boiling products). It must be noted that, in the case of radiolysis at 380° C, the character of the process suffered a qualitative change, acquiring characteristics similar to those of pyrolysis process at 420° C (violent liberation of gas and precipitation of insoluble particles). Another interesting fact is that precipitation of insoluble particles cannot be observed at once, but but only upon concentration of high boiling products on the order of 15 - 20 %. An elementary analysis of these particles has shown that their atomic ratio of carbon to hydrogen is 1.76 .

On this basis, and because of the nature of the insoluble product, we can assume that its basic composition consists of condensed aromatic compounds.

Of real interest is the regularity of change in the average molecular weight of high boiling product with increased doses of exposure of monoisopropyldiphenyl at various temperatures, observed in the course of the experiments. This is illustrated by Fig. 3. Irradiation at low temperatures produces an almost linear increase in the molecular weight of the high boiling product with an increase in dosage. At the same time, with radiolysis taking place at 370° C, the molecular weight of high boiling products decreases with the dosage, approaching a certain state of equilibrium, close to the molecular weight of tetraphenyl. Characteristically, an extrapolation of both curves toward a zero dosage produces the same molecular weight, equal to twice that of the original product. Obtained ratios of the yield of high boiling product and of its molecular weight to the temperature of radiolysis is inescapably tied to the effect of a decline in concentration of high boiling product and of its molecular weight during thermal treatment of the irradiated monoisopropyldiphenyl (see Figures 4 and 5). Investigation of the kinetics of the process of diminishing concentration of high boiling products in this case indicates the existance of a monomolecular mechanism. Apparently there is a thermal destruction of the least stable component of the high boiling product. These results are in close qualitative agreement with the data obtained by De Halas [2].

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[2] De Halas, Radiolytic and pyrolytic decomposition of organic coolants for reactors. Report No. 611 of the First General Conference for Peaceful Uses of Atomic Energy.

Propylamine benzene, investigated by B.A.Medzhibovskiy, is also a mixture of alkyl - displaced polyphenyls, based, apparently, on products whose molecule contains 2 phenyl rings, interconnected by an isopropylic bridge and which has additional marginal alkylic groups. This product has a 310 - 365° C boiling point and an average molecular weight of 214. It is stable thermally up to 375 - 400° C. Radiolysis of propylamine benzene specimens took place in the reactor of the First Nuclear Electric Power Station and, due to the fact that the reactor's channel was not equipped with dosimeters, indicator specimens of monoisopropyldiphenyl were used in all the experiments to obtain comparable data.

In these tests specimens of propylamine benzene and of monoisopropyldiphenyl were irradiated at various temperatures by an integrated flux of thermal neutrons on the order of 10^{18} I/cm^{2} (the period of irradiation was about 20 hours). The data obtained agreed qualitatively with the ratio of yield of high boiling products to the temperature of radiolysis, determined through experiments carried out by U.N.Aleksenko and V.A.Khramchenkov. In addition, they furnished the basis for the assumption that the nature of this relationship (including the area of reduced yields) is more or less typical of alkyl - derived polyphenyls and that it points toward the formation of thermally unstable products of radiolysis. (See Table 1).

Measurements of yields of gaseous products of radiolysis have shown that for monoisopropyldiphenyl and for the propylamine benzene the values are nearly the same and are approximately 0.03 - 0.04 molecules/100 electron-volts . The composition of gaseous products depends upon the integral dosage of irradiation and changes with an increase of the latter toward a comparative impoverishment of the hydrogen composition and its enrichment in gaseous hydrocarbons (with small dosages the hydrogen content reaches approximately 85%, with dosages on the order of several thousands of megarads it drops to 60 - 65 %).

This regularity has been observed on many occasions in the reports of investigations of radiolysis of various polyphenyls and of their derivatives made by other investigators. This leads us to believe that, apparently, today there is a real opportunity to utilize wastes or by-products of a number of chemical processes, involving alkylization of aromatic compounds, for the production of organic coolants.

Studies of K.P.Lavrovskiy, A.M.Brodskiy, N.V.Zvonov, U.N.Aleksenko, V.A.Khramchenkov and others have included investigations of radio - .-thermal stability of hydroterphenyl, a product of selective hydration of vat residues in the production of diphenyl, which are fundamentally a mixture of isomers of terphenyl (the technology of selective hydration was developed by an Associate Member of the Academy of Sciences of the USSR, K.P.Lavrovskiy and his associates).

TABLE I

High boiling products content of specimens of propylamine benzene and of monoisopropyldiphenyl irradiated by an integral flux of thermal neutrons 10^{18} I/cm^2 at various temperatures (in % by weight)

Product irradiated	Temperature of radiolysis °C				
	260	300	350	375	390
Propylamine benzene	7.7	4.57	3.56	2.28	3.38
Monisopropyldiphenyl	-	5.94	3.85	4.5	5.16

This coolant is a mixture of compounds whose molecules are various combinations of petroleum and aromatic rings with a heavy predominance of the latter (the average number of aromatic rings per molecule is 1.62 and of petroleum ones 0.96; the total content of aromatics amounts to 89.5 %) and is characterized by the following parameters:

Melting point	- 11° C
Boiling point	250 - 370° C
Vapor pressure @ 350° C	2.93 kg/cm^2

Cyclohexyldiphenyl is the basic component of the mixture.

Investigations of the pyrolytic stability have shown that the purely thermal influence leads chiefly to the destruction of hydroterphenyl and the formation of gaseous and low boiling products. The pyrolysis, in this case, proceeded at a slow rate up to temperatures in the order of 420 - 450° C. There was no evidence of formation of insoluble precipitates. Experiments with radiolysis of hydroterphenyl were performed in the VVR - 2 reactor, under both the ampoulic and loop conditions. Irradiations at room temperatures produced a straight line increase in concentration of high boiling product with increased exposure, while the speed of the process was characterized by a radio-chemical yeield

$$G_{\text{high boiling product}} = 0.437 \frac{\text{molecules}}{\text{100 electron volts}}$$

(The curve depicting accrual of high boiling products is shown in Fig. 6). At the same time, the molecular weight of the high boiling product increases non-linearly, showing a tendency toward saturation at approximately 700 units. Formation of low boiling product under such conditions does take place, but only to an insignificant extent. In the case of radiolysis at 360 - 380° C formation of gaseous products, similarly to the case of room temperatures, is characterized by the constant

$$G_r = 0.39 \frac{\text{molecules}}{\text{100 electron volts}}$$

however, with lengthening of the exposure, there is a noticeable change in the composition of gases, tending toward a decreased concentration of hydrogen and an increased concentration of gaseous hydrocarbons. (Concentration of hydrogen for a dose of 200 megarads represents 84.5 %, and for a dose of 1600 megarad - approximately 62%. Concentrations of methane and of ethane with ethylene, for a dose of 200 megarad, are 5.9 and 7 % respectively, and at 1,600 megarad - 13 and 11.5 %. In addition, penthane begins to appear in the mixture, beginning with a 1000 megarad dose, while it cannot be detected at smaller dosages). Formation of high boiling and low boiling products and of unsaturated hydrocarbons in the case of radiolysis at high temperatures is characterized by a sudden decrease in yield with increased radiation doses (curves showing the relation of yields to dosages are shown in Figure 7, 8 and 9). It should be noted that, during the experiments with hydroterphenyl (during both its pyrolysis and radiolysis), there was no perceptible precipitation of insoluble products and no evidence of condensed aromatic, which is a most important consideration, from the standpoint of its practical utilization.

On the basis of the above findings we conclude that, in the case of the radio- -thermal treatment of hydroterphenyl, dehydrogenation and cracking occur concurrently with condensation. What is more, it appears that the first two processes are caused primarily by the thermal effect, which explains the decreased yield of high boiling product when radiolysis takes place at higher temperatures.

Finally, a third type of organic composition investigated as a possible organic coolant was the hydrostabilized kerosene- gas oil petroleum fraction, which is a complex mixture of aromatic, petroleum and paraffin hydrocarbons. Investigations of hydrostabilized gas oil were made concurrently with those involving hydroterphenyl, by the same authors. Hydrostabilized gas oil can be characterized by the following parameters:

Melting point	- 60° C
Boiling point	200 - 350° C
Average molecular weight	200
Aromatic component content	up to 35% (by weight)

Pyrolytic investigations of hydrostabilized gas oil revealed that, up to 400° C, progress of thermal decomposition is very slow and leads to the formation of both high and low boiling products. In the course of this, formation of high boiling product progresses non-linearly with respect to time and trends toward saturation. The level of saturation becomes lower with increased temperatures of pyrolysis (from approximately 3% at 200° C to 1% at 350° C). At 400 - - 420° C the progress of pyrolysis assumes the characteristics of the cracking process and is accompanied by both a sudden increase in gas liberation and an increased rate of formation of high boiling product. Radiolysis of hydrostabilized gas oil, similarly to that of hydroterphenyl, is characterized by formation of gases, low boiling product, high boiling product and intermediate hydrocarbons, but the quantitative natures of the processes are very different. In the case of hydrostabilized gas oil accumulation of high boiling product in radiolysis trends toward saturation even at room temperature, which produces a noticeable decrease in the yield of radio - - chemical high boiling product as its concentration increases (Fig. 10).

When the temperature of radiolysis is increased to 250- - 300° C, there is a gradual increase in yield of high boiling product and of gaseous products. At the same time, activation energies for both processes are almost equal.

Further increase in the temperature of radiolysis leads to a sudden change in the nature of the process: activation energy for the speed of gas formation increases abruptly, while the yield of high boiling product begins to decline just as rapidly, which indicates a preponderance of an intensive destructive process in that temperature range (the curves showing relation of temperatures to the initial yields of high boiling and gaseous products are shown in Figures 11 and 12). This nature of the temperature relation indicates the start of a typical cracking process. Considering that, due to a purely thermal effect, cracking of hydrostabilized gas oil begins at approximately 400° C, we can state that in this case we are dealing with a sharply defined radiational-thermal cracking, that is, with a lowering of the temperature threshold of cracking, produced by radiation. A very abrupt lowering of the yield of high boiling and gaseous products with increases of the integral dose are typical of irradiation of hydrostabilized gas oil at high temperature, as well as of its irradiation at room temperature.

Figures 13 and 14 show the relationship of the yield of high boiling products and gases to the dose, obtained during irradiation of hydrostabilized gas oil at 330° C (this temperature appears at present to be the maximum possible one for the use of hydrostabilized gas oil as a coolant). The paths of the curves in these graphs differ noticeably: decline in the yield of high boiling products with the dose progresses quite uniformly, while liberation of gases has an area of abrupt decline at relatively small doses. This result is in close agreement with the data obtained in the analysis of exposed gas oil, in which we obtained an abrupt decrease in paraffin hydrocarbon content and a slower decrease of petroleum fractions, accompanied by a certain increase in aromatics. The preeminent radiolysis of paraffin components, which, as we know, leads basically toward a destructive process with a massive liberation of gases, is apparently the cause of the strong liberation of gases at the start of radiolysis of gas oil and its subsequent rapid decline at comparatively low dosages. Subsequent decrease of radiolytic yields is apparently caused by the lowered concentration of petroleum and a higher concentration of aromatic hydrocarbons. Consequently, because of the amounts of initial yields of products of radiolysis, hydrostabilized gas oil appears to be unsuitable as a reactor coolant, however, even in the initial stage of radiolysis, its properties improve radically and become quite acceptable. Advantages offered by hydrostabilized gas oil are the absence of formation of condensed aromatics and of insoluble products. The comparatively low cost and availability of this coolant also make its use most attractive.

As mentioned previously, concurrently with investigations of radiation stability of organic coolants, K.P.Lavrovskiy, A.M.Brodskiy, D.V.Makarov and A.N.Mezentsev have initiated the development of the most effective method of regeneration of products of radiolysis. The goal of this series of studies was to find the effective means of decomposing the high boiling products and of simultaneous hydration of unsaturated hydrocarbons, since the latter have a strong tendency toward radiation polymerization, which can lead to the formation of insoluble products and tar coatings on the heat radiating surfaces. (Elimination of gaseous and low boiling products presents no serious problems). To accomplish this, we decided to employ destructive hydrogenation, in the course of which we could insure, through the selection of a suitable catalyzer and process regime, the destruction of high boiling products and hydration of the unsaturated, without appreciable decomposition of the aromatic components of the coolant. Laboratory tests have shown that the course of such a process can be insured with the use of the alumocobaltomolibdenic catalyzer, commonly used in petroleum chemistry, at temperatures of $300-400^{\circ}$ C and hydrogen pressures of 40-60 atmospheres (the required temperature declines as the hydrogen pressure increses). To check our solution, we constructed a loop type regenerative installation (Fig. 15), whose continuous operation was tested at the time of the loop experiment with hydroterphenyl. This apparatus functioned under the following regime:

hydrogen pressure	60 atmospheres
temperature in reactor	320° C
molar ratio of circulation of hydroterphenyl to that of hydrogen	1 : 6

Figure 16 presents the curves depicting changes in the concentration of high boiling product and of unsaturated hydrocarbons within the circuit of the loop during continuous regeneration and subsequent to its termination. The results obtained completely confirmed the effectiveness of our method of regeneration. The advantage of this method lies in the fact that a regenerative installation of this type can operate continuously on the by-pass line of the nuclear power installation circuit, since it does not require preliminary removal of high boiling products and unsaturated hydrocarbons from the coolant. Employment of this, or a similar method of regeneration of organic coolants substantially broadens the number of suitable organic compositions, since the method imposes lower requirements on their radiation stabilities.

In addition, the problem of transportation and subsequent disposal of high boiling products, which invariably arises with the use of distillational purification, [illegible] almost non-existant in this case (it is most important that distillational cleaning does not solve the problem of removal of unsaturated hydrocarbons from the circuit and those, as stated before, together with high boiling products are very undesirable). It should also be noted that development of this method of regeneration permits the use of inexpensive hydrostabilized gas oil as a coolant in the "Arbus" plant, which renders it equal to the more radiationally stable coolants, on the basis of comparative cost indexes.

THERMO - PHYSICAL INVESTIGATIONS

Investigations of heat transfer characteristics of organic coolants were performed basically along these lines:

1) Investigation of the general mechanism of convective heat exchange during induced flow of an organic fluid;

2) Investigation of crisis of heat removal during the surficial boiling of an organic fluid;

3) Investigation of the effect of radiolysis on the heat transfer characteristics of a coolant.

During the series of experiments relating to convective heat exchange, performed by U.N.Aleksenko and N.I.Propletin, using monoisopropyldiphenyl and hydrostabilized gas oil, it was demonstrated that the results with an accuracy of ± 20% are circumscribed by the well known Kraussold criterial formula. (The results of these measurements are depicted in the graph of Fig. 17). A similar result was obtained also with monoisopropyldiphenyl with a high boiling product content on the order of 10%. More painstaking investigations performed by L.S.Sterman and V.V.Petukhov showed that, for a more accurate calculation of heat emission to monoisopropyldiphenyl and diphenyl, for various ranges of parameters of the process, it is necessary to use various modifications of criterial expressions of the same type.

Experimental work of U.N.Aleksenko, I.N.Vasilyev and B.E.Yaroslavtsev, related to changes in the thermo-physical parameters of monoisopropyldiphenyl, hydrostabilized gas oil and hydroterphenyl during radiolysis has revealed that the effect of radiolytic change on the composition of organic coolants varies greatly, depending upon the nature of the original product and associated specifics of the radiolytic processes. In the case of monoisopropyldiphenyl, characterized by the formation of only gaseous and high boiling products in the course of radiolysis, some general rules were observed.

Specifically, it was established that the density of monoisopropyldiphenyl, as a function of the temperature and high boiling product content, can be described with sufficient accuracy by the following expression:

$$\gamma(t,c) = \gamma_{20}(c)\left[1-\alpha(c)(t-20)\right],$$
$$\gamma_{20}(c) = 0.981 + 0.65\cdot 10^{-3}\cdot c,$$
$$\alpha(c) = 0.8\cdot 10^{-3} - 2.5\cdot 10^{-6} c,$$

where γ - density in grams / cm^3

C - concentration of high boiling product in %.

It should be noted that the experimental results are well described by this formula, regardless of the temperature prevailing in the process of radiolysis (from room temperature to 300° C).

Measurements of the thermal capacity of monoisopropyldiphenyl disclosed that the thermal capacity of the mixture does not differ from that of the original product by more than 5 %, for any concentration of the high boiling products between 0 and 100 %.

Effects of high boiling products on the viscosity of monoisopropyldiphenyl appear to be more complex, due to the greater sensitivity of this characteristic with relation to the composition of the created high boiling products.

The latter, as mentioned before, depends to a large extent on the temperature of radiolysis. In addition, it was found that change in the temperature of radiolysis leads not only to a change in the absolute value of viscosity for an equal high boiling product content, but to a change in the activation energy of the thermal viscosity ratio. For the practically interesting range of radiolysis temperatures of 200 - 350° C, relation of viscosity to the temperature and high boiling products content can be described by the following expression:

$$\eta(T,C) = 1.4\exp\left\{\left[\frac{3.6+0.028C}{R}\left(\frac{1}{T}-\frac{1}{373}\right)10^{3}\right]+0.025C\right\},$$

where η - viscosity in centipoise,

C - concentration of high boiling product in %.

The formula is accurate at temperatures above 100° C (at lower temperatures the relation of viscosity to the temperature deviates from an exponential one, and the higher the boiling product content, the greater the deviation).

In the case of hydrostabilized gas oil and hydroterphenyl, during whose radiolysis there is a formation of substantial quantities of low boiling products of decomposition, along with gaseous and high boiling products, it appears impossible to establish any general quantitative rules for the change in thermo-physical characteristics, particularly because the formation of low boiling products is materially affected by the thermal regime of radiolysis. Even if it were possible to accomplish this on the basis of ampoulic experiments, the results would be of little practical value, since in an actual installation there would inevitably be a partial loss of low boiling product vapors in combination with gaseous products released from the circuit, and there would also be a continuous destructively hydrogenational regeneration of the coolant, without which employment of hydrostabilized gas oil or of hydroterpheryl does not appear justifiable. Because of this, the composition of the coolant circulating in the system will each given case have its own specifics which will to a large extent affect the changes in the thermo-physical characteristics.

Data obtained in the course of the loop experiment with hydroterphenyl indicate that, with a proper selection of the thermal regime of radiolysis and the regime of removal of gases and regeneration, which determine the relative concentrations of high and low boiling products in the coolant, it is possible to achieve a stability, or even a certain improvement of the heat transfer characteristics of a coolant subjected to radiolysis.

Investigations of critical thermal loads for organic coolants were performed by L.E.Mikhaylov and K.V.Naboychenko (experiments in a ring gap with an inside diameter of 6 mm and an external one of 10 mm). and by L.S.Sterman and V.D.Mikhaylov (experiments in a tube). For the first series of experiments, using monoisopropyldiphenyl at pressures of 2 - 9 atmospheres, velocities of 2 - 8 M / sec and fluid temperatures of 100 - 300° C, and for those with benzene at pressures of 2.5 - 40 atmospheres, velocities of 4 - 21 M/sec and temperatures ranging from room temperature to saturation at each pressure, all results were adequately (with an accuracy of ± 20 %) described by the generalized formula [3].

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[3] L.E.Mikhaylov. Generalization of certain tests of the crisis of boiling of a fluid during induced flow on the basis of thermodynamic similarity. Journal of Applied Mechanics and Technical Physics No. 3, p. 130 (1963).

$$\frac{q_{kp}}{P_K W_K} = 3\cdot 10^{-4}\left(1-\frac{P}{P_K}\right)\left(1+6.7\frac{\Delta i}{\tau}\right)\left[1+0.8\left(10^2\frac{W}{W_K}\right)^{0.8}\right]$$

q_{kp} - critical thermal loading in $\frac{\text{kilocalories}}{\text{M}^2\ \text{hour}}$

P, P_K - pressure and critical pressure in atmospheres

W, W_K - velocity of fluid an velocity of sound at the critical point in M / sec.

τ - latent heat of evaporation in kilocalories / kg

Δi - underheating of the fluid up to saturation in kilocalories / kg.

The graph of Fig. 18 represents the correlation in accordance with the above formula, of the results of the monoisopropyldiphenyl test at 5 atmospheres.

Studies of L.S.Sterman and V.D.Mikhaylov covered the crisis of heat extraction for monoisopropyldiphenyl, deuterium and diphenyl in the pressure range of 0.035 - 0.33 of the critical pressure, underheat of fluid range of 0 - 200 °C and velocities of 4 - 15 M / sec. The tests were made in tubes with a 10 mm inside diameter. L.E.Mikhaylov's processing of these results in accordance with the above formula also produced a satisfactory correlation. However, the authors of these latter experiments recommend the use of a system of formulas adapted to a more precise calculation of critical thermal flows. Applicability of each one of these formulas is limited by a definite range of input parameters. For example, in order to calculate the critical thermal load at zero underheat of the fluid, the use of the following expression is recommended:

$$\frac{\dot{q}_{\kappa p}}{r\sqrt{g\gamma''}\sqrt[4]{\sigma(\gamma'-\gamma'')}} = 0.0145\left(F_r\frac{\gamma'}{\gamma''}\right)^{\frac{1}{4}},$$

where σ - surface tension of the fluid,

γ', γ'' - fluid and vapor densities,

$F_r = \dfrac{w_0^2}{g\sqrt{\dfrac{\sigma}{\gamma'-\gamma''}}}$ - Frud's criterion.

This formula applies in the range of values of the complex

An examination of the results of these measurements shows that an achievement of thermal loading in the order of $10^6\ \dfrac{\text{kilocalories}}{\text{M}^2\ \text{hour}}$ appears quite feasible, when surficial boiling is utilized in the process of heat extraction with the aid of organic coolants. This fact is most important from the standpoint of the possibility of increasing the reduction of energy levels of reactors with the aid of organic coolants.

NEUTRON - PHYSICAL STUDIES

Due to the fact that organic fluids under investigation are typical hydrogen - containing moderators with nuclear densities of hydrogen, sufficiently close to those of water, in computing the parameters of multiplication of the [illegible] of organic reactors, the logical approach was to resort to the methods and programs of machine computing, developed and tested for water systems. The correctness of this assumption was confirmed by experimental results of V.I.Mostovoy, V.S.Dikarev and others, related to the comparative study of neutron spectra in uranium-monoisopropyldiphenyl and uranium-water lattices [4]. According to this data, the monoisopropyldiphenyl lattice is equivalent to that of water, with a smaller pitch, which corresponds to the smaller nuclear density of hydrogen in the mon isopropyl - diphenyl. The spatial distribution of neutrons in these two systems must also be identical, for the same ratios of nuclear densities of uranium and hydrogen. But, in view of

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4. V.I.Mostovoy, V.S.Dikarev and others. Measurement of neutronic spectra in uranium-water and uranium-monoisopropyldiphenyl lattices. Atomic Energy, Vol. 13, 6-th Edition, p. 547 (1962).

the fact that development of correct calculating programs called for an input of a system of constants applicable to a broad class of organic moderators and also, taking into account certain fluctuations of the elementary composition of even the same product in different batches due to slight variations of technological parameters of production, and the change in elementary composition during radiolysis, it became necessary to develop a set of general rules for the change of constants, depending upon the correlation of the hydrogen and hydrocarbon content.

The tendency toward a maximum increase in power intensity of the core and comparatively low heat transfe characteristics of organic fluids create the need for all possible development of the specific surface of heat release per unit volume of the core. This consideration calls for selection of lattices with a comparatively tight pitch in the design of organic reactors. In this connection, in the course of our neutron-physical studies, special attention was devoted to the determination of the square of the length of moderation of neutrons, a constant the exact value of which is of greatest importance in the correct calculation of critical parameters of the ensemble in this series of steps. The graph in Fig. 19 shows the calculated curve of the relation of the square of the length of moderation to the nuclear density of hydrogen, obtained with the aid of the widely-known age technique, corrected for loss of energy during the first collision. To accomplish this we used the 30 - group system of ANL constants [5].

The same graph also shows the experimental magnitudes of the square of the length of moderation for diphenyl, obtained by U.U.Braun [6] and for monoisopropyldiphenyl, obtained by L.N.Yurova in the course of her experimental tests. The figure for hydrostabilized gas oil was obtained indirectly by M.N.Meshcheryakov and I.V.Rogozhkin in processing the results of critical experiments (the experimental points plotted in the graph apply to a density value of 1 gm /cm^3).

Agreement of experimental data with calculated values is quite satisfactory.

Experiments of L.N.Yurova covering the measurement of diffusion of thermal neutrons in diphenyl and in monoisopropyldiphenyl have shown that for all non-crystalline hydrogen-containing substances it is possible to use the calculated data, [illegible]ging the transport cross section of hydrogen

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[5] Handbook of the Argonne National Laboratory Reactor Physics Constants ANL - 5800.

[6] U.U.Braun. Exponential tests of an organic moderator. Report No. 595 of the First Geneva Conference.

which is equal to 35.7 barn at 0.0252 electron-volt, according to Maxwell's spectrum. A number of critical tests using monoisopropyldiphenyl and hydrostabilized gas oil as moderators were performed by N.V.Zvonov, Yu.N.Aleksenko, M.N.Meshcheryakov, I.V.Rogozhkin, B.E.Yaroslavtsev and others, in order to verify their assumptions.

The monoisopropyldiphenyl tests were performed on the fuel elements of the VVR-C reactor. Hydrostabilized gas oil tests were made on the fuel elements of the VVR-C and VVR-M reactors. Figure 20 presents the calculated and experimental curves of the relation of the critical loading of the assembly for the monoisopropyldiphenyl tests to the lattice pitch. As seen from this diagram, calculations produce a very close agreement with the experimental results in the zone of tight lattices. In the zone of pitches larger than the optimal, the agreement is less satisfactory. The same rule prevailed in the hydrostabilized gas oil tests.

The results of the physical startup of the "Arbus" reactor installation, made in the summer of 1963 and covered by a separate report, also furnished excellent confirmation of our adopted calculating techniques and constants, at least for cores with use of lattice pitches not much greater than the optimal ones.

INVESTIGATIONS OF STABILITY OF MATERIALS IN ORGANIC COOLANTS

The question of interaction of heat-liberating and structural materials with organic coolants appears to be very complex, since under actual operating conditions the process of chemical interaction of these materials is inevitably associated with a whole complex of physical-chemical processes. It is also necessary to take into account the radiolytic and pyrolytic reactions in the coolant, interaction of their products with a given material, corrosive effect of the coolant and of its admixtures on the material and finally, the effect of the material itself and of its products of corrosion on the physical-chemical processes within the coolant. Investigations relating to this problem were carried out simultaneously along several lines. The work of A.N.Razinov, Yu.F. Bychkov and I.D.Laptev consisted of studies of interaction of a number of pure metals and of their combinations with products of pyrolysis of diphenyl.

The tests were performed at temperatures of 370°C, 410°C and 450°C, thus they covered both the pre-cracking area and the area of pyrolytic cracking. The specimens to be investigated were in powdered form.

The results of the tests performed on non-fissionable materials appear in Table II. The Table shows that of all of the pure metals investigated only aluminum, iron and titanium can resist the effects of pyrolitic hydrogen generated. However, titanium is subject to carbidization, which progresses visibly even at 370° C.

Among oxides investigated the only unstable one was MoO_3 which, placed in an organic medium, undergoes deoxidation accompanied by formation of molibdenum carbide.

A number of heat-producing compositions were subjected to similar tests. Table III presents the basic results of this series. Results show that uranium dioxide and uranium carbide are completely stable, among all the uranium compounds tested under the given conditions. Metallic uranium becomes completely hydrated by pyrolytic hydrogen at 370°C. With an increase of temperature there is a transition from hydrate to carbide and at 450°C virtually the entire specimen is transformed into uranium carbide. U_3O_8 is partially transformed by pyrolytic hydrogen into uranium dioxide which, as mentioned above, is a completely stable compound under the existing conditions.

In the series of tests performed by K.N.Nikitin, testing conditions of samples approached the actual ones. (The experiments were made in industrial diphenyl with a 0.014 % water content and in monoisopropyldiphenyl with a 0.025 % water content; industrial nitrogen with an oxygen content up to 0.5 % was the inert atmosphere in the ampoules; material samples were not powders, but were cut from a sheet). The purpose of this series was investigation of corrosion of the

Table II

Chemical Interaction of Some Non-fissionable Materials with Diphenyl

Material investigated	Temperature of test (°C)	Length of test (hrs)	State of material after test
1	2	3	4
Al	4I0	540	Al
Fe	450	240	Fe
	4I0	540	
	370	500	
Ta	450	240	TaH
	4I0	540	
	370	500	
Nb	450	240	NbH
	4I0	540	
	370	500	
Zr	450	240	ZrH
	4I0	540	
	370	500	
Ti	450	240	TiC
	4I0	540	Ti + TiC
	370	500	Ti + TiC
ZrO_2	450	240	ZrO_2
	4I0	540	
	370	500	
ZrH	450	240	ZrH
	4I0	540	
	370	500	
TiO_2	450	240	TiO_2
	4I0	540	
	370	500	

Material investigated	Temperature of test ($^{\circ}$C)	Length of test (hrs)	State of material after test
1	2	3	4
Ta_2O_5	450	240	Ta_2O_5
	410	540	
	370	500	
Nb_2O_5	450	240	Nb_2O_5
	410	540	
	370	500	
Cr_3O_2	450	240	Cr_2O_3
	410	540	
	370	500	
MoO_3	410	540	$MoC + MoO_3$

Table III

Chemical Interaction of Some Fissionable Materials and Diphenyl

Material investigated	Temperature of test (°C)	Length of test (hrs)	State of material after test
U	450	240	UC
	4I0	540	$UH_3 + UC$
	370	500	UH_3
UO_2	450	240	UO_2
	4I0	540	
	370	500	
U_3O_8	450	240	UO_2
	4I0	540	
	370	500	
UC	450	240	UC
	4I0	540	
	370	500	

same non-fissionable metals which were subjected to the tests described above, also of IXI8N9T chrome-nickel stainless steel and of zirconium alloy. In these tests the specimens remained in the organic medium for 500 hours at a temperature of 400°C. This testing assignment included clarification of the nature of the resulting products of corrosion and of their effect on the pyrolytic process of the coolant.

Under these conditions, the specimens investigated showed the following increases in weight, which characterise their tendency to corrode:

Aluminum, stainless steel and titanium	0.06 mg/cm^2
Niobium and tantalum	0.3 mg/cm^2
Zirconium and zirconium alloy	0.4-0.8 mg/cm^2

Corrosion of magnesium and iron was accompanied by a decrease in weight of the specimen and transition of products of corrosion into the medium. In the course of the experiments, the nature of corrosion of materials investigated differed widely. Similarly to the previous series of tests, it was demonstrated that destruction of zirconium, zirconium alloy, niobium and tantalum takes place due to the formation of hydrates of these materials. At the same time, no increase in hydrogen content could be detected in stainless steel, aluminum and titanium specimens. Their corrosion is governed entirely by oxidizing processes which, apparently, take place due to presence of water and dissolved oxygen in the organic fluid. As mentioned before, products of oxidation of magnesium and of iron blend readily with the organic medium, fouling it, and are thus very active catalyzers in the pyrolytic decomposition of the medium (especially magnesium oxide). In contrast, products of oxidizing corrosion of aluminum produce a tight film on the surface of the specimen and are catalytically passive. Tests have shown that there is a complete correlation between the catalytic activity of the products of corrosion and the intensity of deposition of insoluble products of pyrolysis on the surface of a specimen. This was also confirmed on specimens placed in the experimental channel of the organic circuit of the VVR-2 reactor, in a medium of hydroterphenyl and gas oil, that is, in the presence of radiolytic decomposition of the organic coolant. And so, on the basis of these tests, we consider aluminum-based materials to be the most suitable coatings for organic reactor heat liberating elements.

A series of tests performed by A.A.Nevzorova investigated the comparative stability of various aluminum based alloys under ampoulic conditions. These tests were made in gas oil at 330°C, in monoisopropyldiphenyl at 350°C and in hydroterphenyl at 370°C. Exposures of specimens varied from 1,000 to 5,000 hours. These tests demonstrated, first of all, that the general rules of the process of interaction of materials investigated with the medium were the same in all three cases, although the rates of corrosion of all specimens placed in the above three media were different. The ratios for gas oil, monoisopropyldiphenyl and hydroterphenyl were 1:0.5:0.3, respectively (the rate of corrosion was determined from the weight increase of the specimens). Although all the specimens of alloys investigated showed a fully satisfactory corrosional resistance, it was observed that there was some difference in the effect of alloying admixtures.

The strongest corrosion was observed on specimens with admixtures of zirconium, nickel and molybdenum. On specimens with magnesium additions there were no appreciable weight changes, but a microstructural analysis disclosed the presence of a noticeable intercrystalline corrosion and, during the 3,000 hours of the experiment, the depth of cracks of some specimens reached 120 microns. The nature of this intercrystalline corrosion has not yet been clarified no appreciable change in the mechanical properties of the specimens was observed during this experiment. Special tests to determine the effects of water content of the organic medium on the rate of corrosion of aluminum alloys were included in the above series (these tests were made in monoisopropyldiphenyl at 350°C). It was determined that with a 1.0% water content, the rate of corrosion of aluminum alloys increases 100 fold, compared to that prevailing in pure monoisopropyldiphenyl. A 0.5% water content increases the corrosion rate 10 - 20 times.

Finally, with a 0.1% moisture content, the rate of corrosion matches that observed when we used pure monoisopropyldiphenyl (according to the analysis made in pure monoisopropyldiphenyl subjected to an additional distillation, the moisture content was approximately 0.025%). It must be noted that in all of these tests the highest corrosional resistance was that of the control specimens made of pure aluminum, without alloying admixtures, but its mechanical properties at high temperatures seriously limit the possibility of its use.

CONCLUSION

On the basis of results obtained we can affirm that organic compounds of alkyl-displaced or partially hydrated polyphenyl type, as well as various mixtures with sufficiently high aromatic hydrocarbon content, can be readily used as coolants in the primary circuits of nuclear power plants.

It appears possible that we can produce organic coolants of this type by utilizing the comparatively simple reprocessing of by-products or waste products of a whole series of chemical industrial processes. In this connection, the use of destructive regeneration to free the coolant of undesirable products of radiolysis seems currently to be the most progressive means of solving this problem. In this case the number of organic products that can be used as coolants can be substantially increased, since the amount of radio-chemical yield of high boiling product ceases to be the main limiting factor (obviously, within reasonable limits). The positive experience of employing the directly distilled petroleum fraction (hydrostabilized gas oil) as a coolant confirms this assumption. The principal limiting factor of organic coolants is the maximum permissible temperature. Most serious attention should be devoted to the determination of the permissible temperature for each given case, since violation of this limitation can lead to serious consequences (formation of insoluble products, tar coating of hot surfaces, etc.). For the coolants which we have investigated, the following limiting temperatures (for the hottest point of the reactor) are considered applicable:

monoisopropyldiphenyl	350°C
hydroterphenyl	380-400°C
hydrostabilized gas oil	330°C

(For propylamine benzene the available results so far do not permit us to establish a limiting temperature. It seems that it is close to that of monoisopropyldiphenyl).

On the basis of polyphenyls and their derivatives, it does not seem possible to increase the above figures materially. Solution of this problem might be achieved on the basis of elemental organic compounds.

A very pressing problem is that of increasing the specific energy level of the core of organic reactors. Results of investigations of the crisis of heat extraction indicate that, from the thermotechnical standpoint, the use of surficial boiling offers the best prospects in this area. However, from the standpoint of radiation chemistry, the problem remains unsolved, since it is not known what effect such boiling will have on the surfaces of the fuel element, the hottest and strongest reactive part of the core, and on the radiolytic processes within the coolant. This circumstance requires careful experimental checking.

Investigations of corrosive activity of organic coolants show that, for temperatures associated with the use of polyphenyl based fluids, the best coatings for fuel elements are aluminum based alloys or pseudoalloys. As to the choice of structural materials for the equipment and connections of the primary circuit, our scant available operating experience in the use of organic reactors has not as yet refuted the propriety of using conventional carbon steels of the perlite type for these purposes.

However, this problem should be handled with certain caution, considering the catalytic effects of iron oxides on the processes of pyrolysis and radiolysis. In any case, special attention must be devoted to the cleaning of this circuit prior to the introduction of coolant, both before initial operation of a new installation and after completion of overhaul involving drainage of the circuit.

Summarizing everything said before, we can say that in spite of the currently apparent specific features of operations related to the use of organic coolants, nuclear power plants employing organic reactors must be considered to be very promising from the economic standpoint. Their use in low-power installations appears especially expedient, for in such cases the capital component of the cost of electric power plays an especially important role.

Fig.1. Rate of accumulation of high boiling product in monoisopropyldiphenyl for various temperatures of radiolysis.

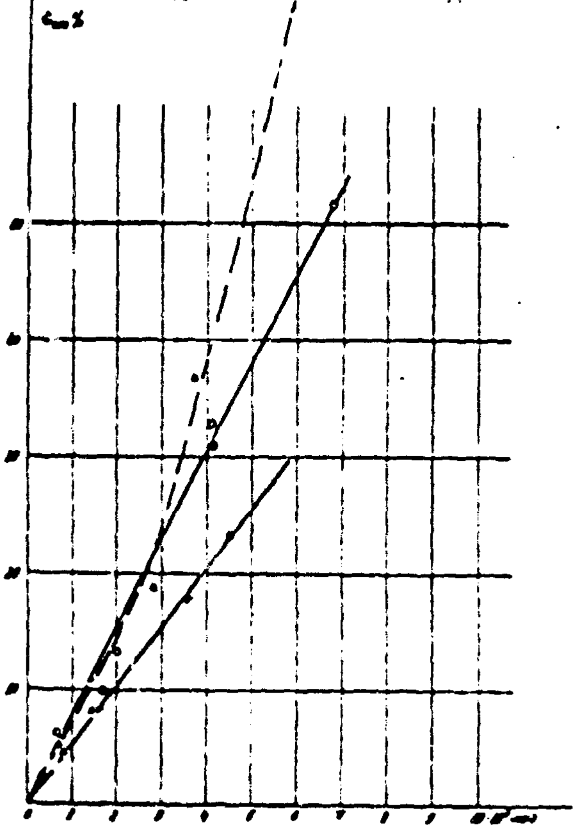

Рис. I. Ход накопления ВК в МИПД при различных температурах радиолиза.

● - 50°C ; X - 200°C ;
⊡ - 300°C ; ▲ - 380°C.

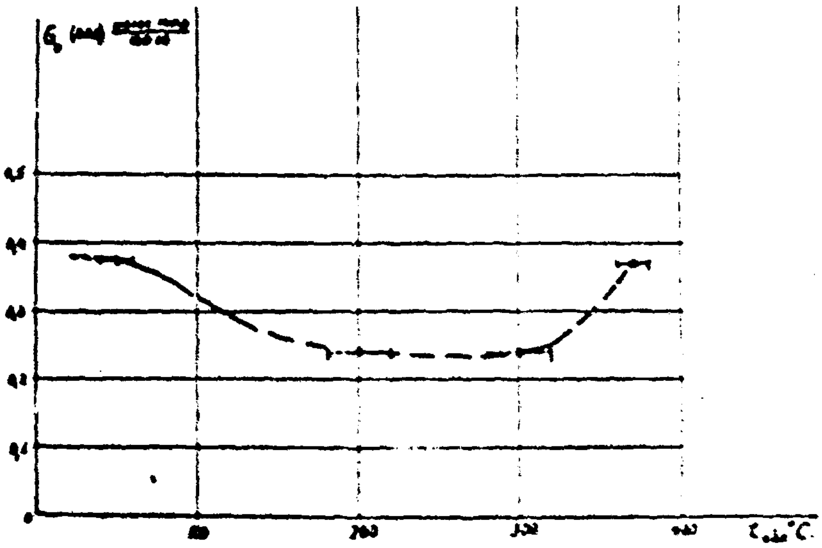

Fig.2. Change in yield of high boiling product with radiolysis temperature of monoisopropyldiphenyl.

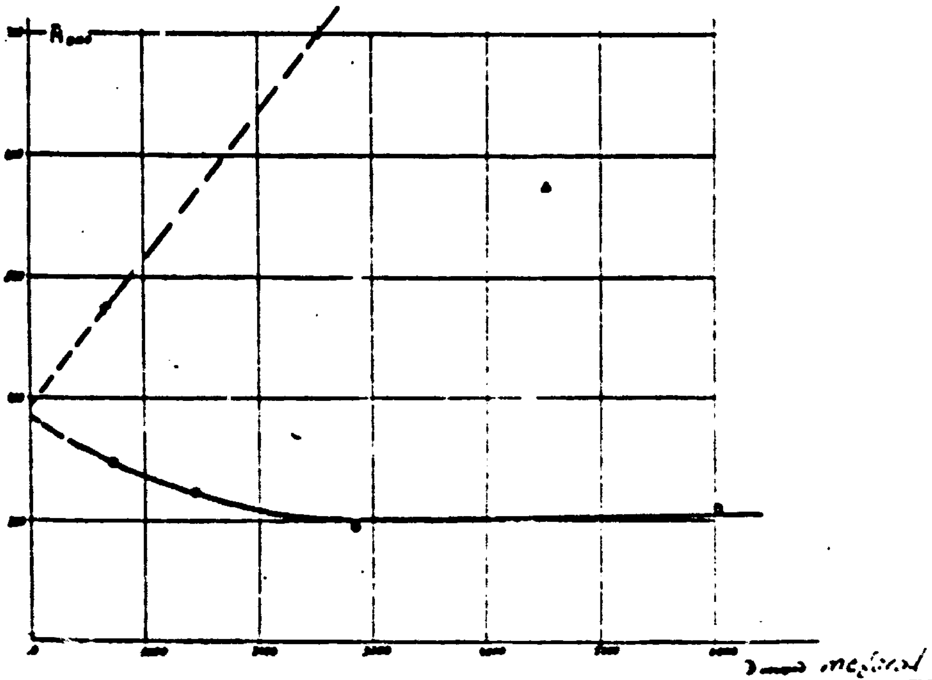

Fig.3. Change of mean molecular weight of high boiling product during radiolysis of monoisopropyldiphenyl.

x - temperature of radiolysis 50°C
Δ - " " " 200°C
⊙ - " " " 380°C

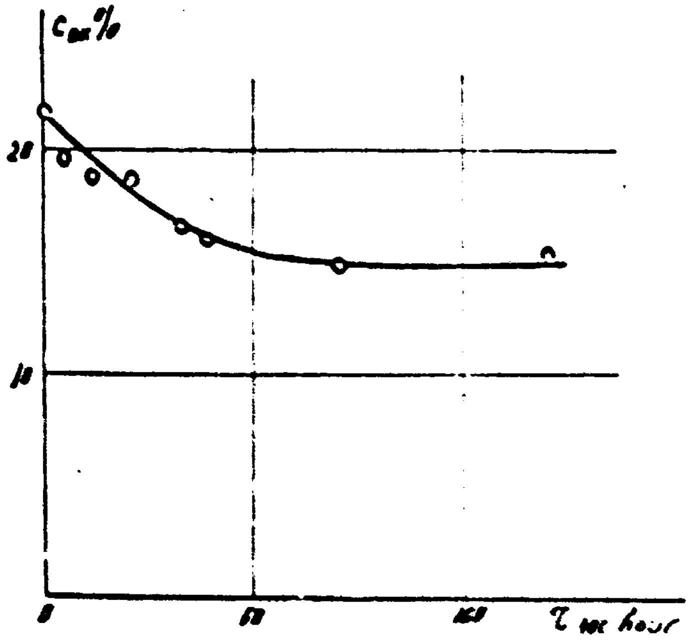

Fig.4. Drop in concentration of high boiling product during thermal treatment of previously irradiated monoisopropyldiphenyl. (Radiolysis temperature - - 200°C; thermal treatment at a temperature of 350°C).

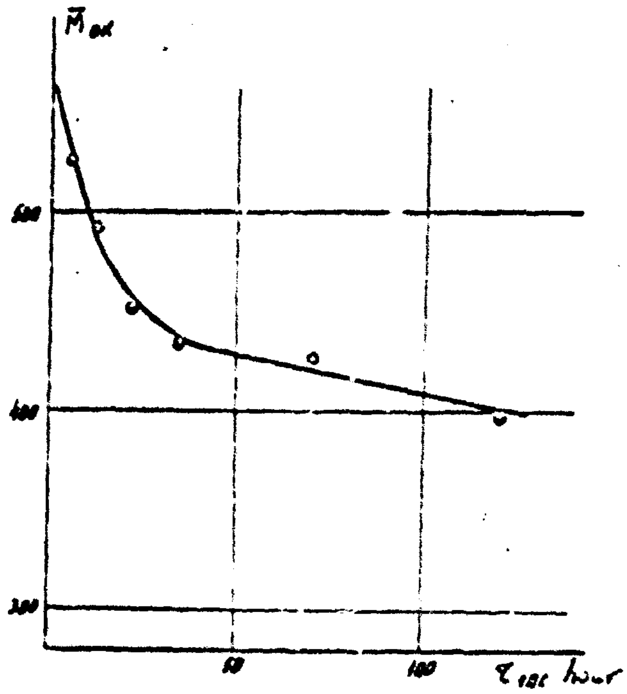

Fig.5. Lowering of mean molecular weight of high boiling product during thermal treatment of previously irradiated monoisopropyldiphenyl. (Radiolysis temperature - 200°C, thermal treatment at 350°C).

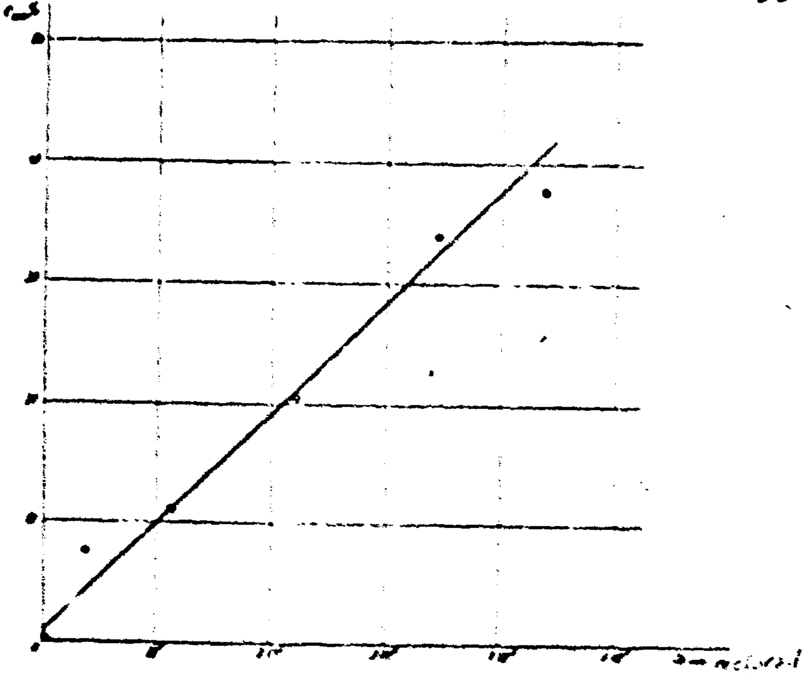

Fig.6. Progressive accumulation of high boiling product in hydroterphenyl at room temperature of radiolysis.

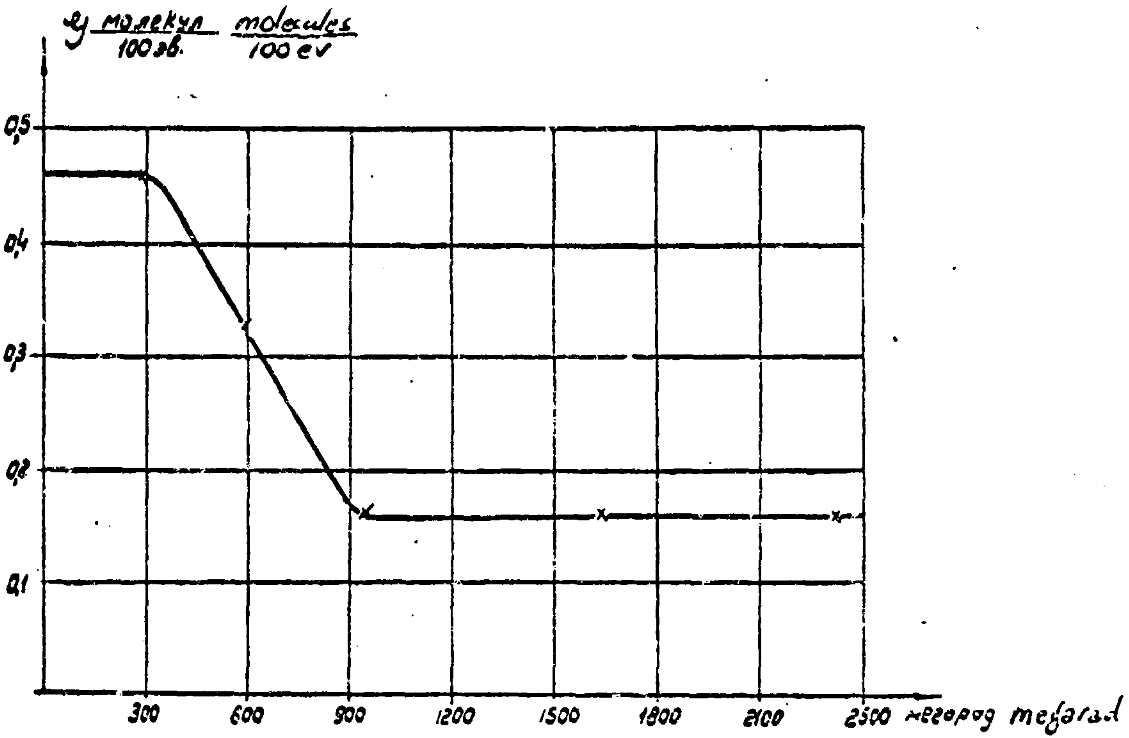

Fig.7. Change in yield of high boiling product in hydroterphenyl with the irradiation dosage at a radiolysis temperature of 380°C.

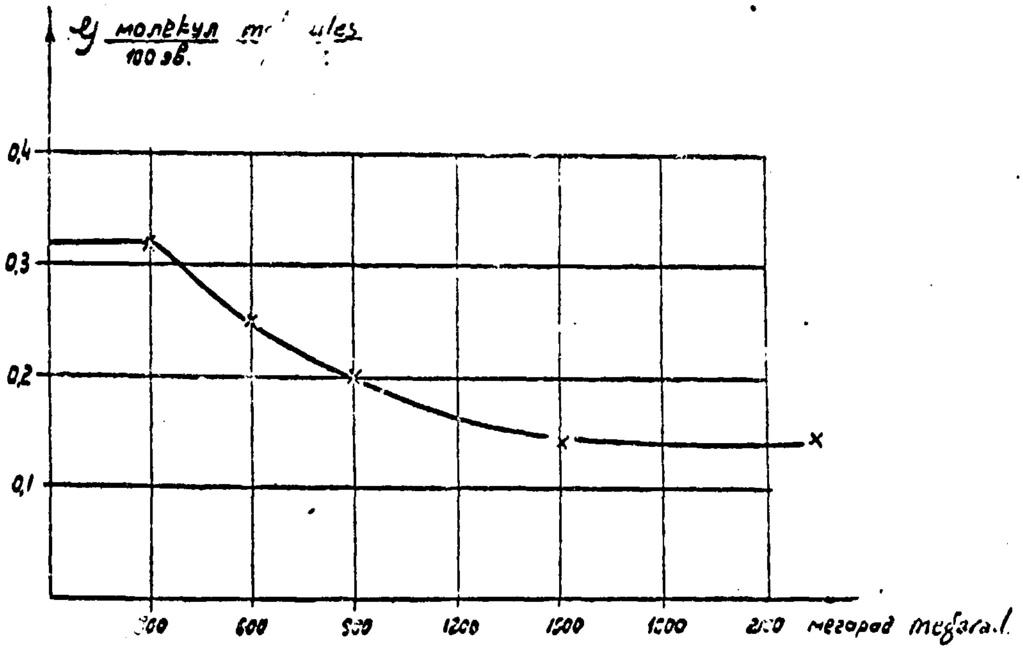

Fig.8. Change of yield of low boiling product in hydroterphenyl with the irradiation dosage at a radiolysis temperature of 380°C.

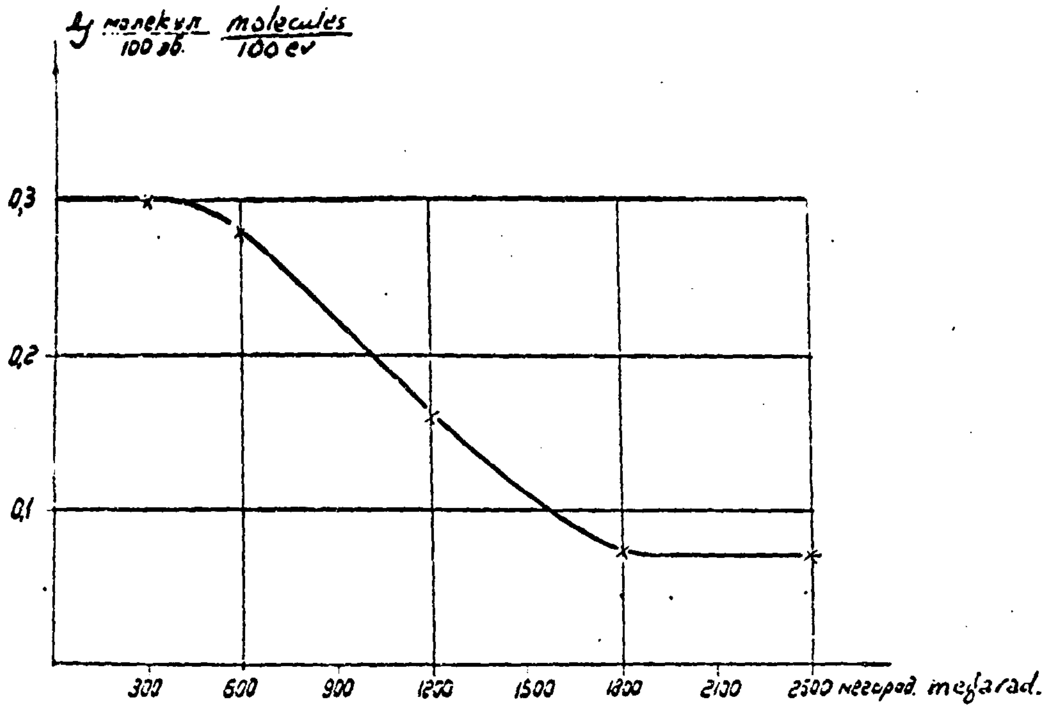

Fig.9. Change of yield of unsaturated hydrocarbons in hydroterphenyl with the radiation dosage at a radiolysis temperature of 380°C.

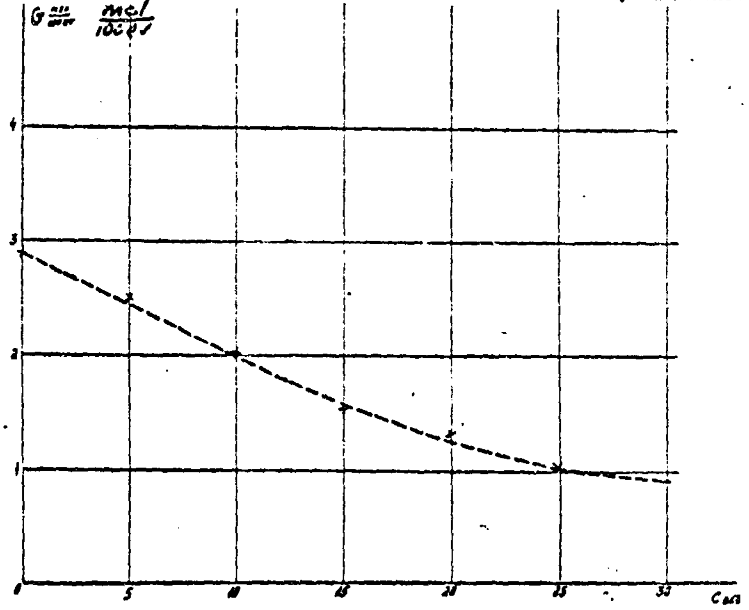

Fig.10. Change of yield of high boiling product in hydrostabilized gas oil with the irradiation dosage at room temperature of radiolysis.

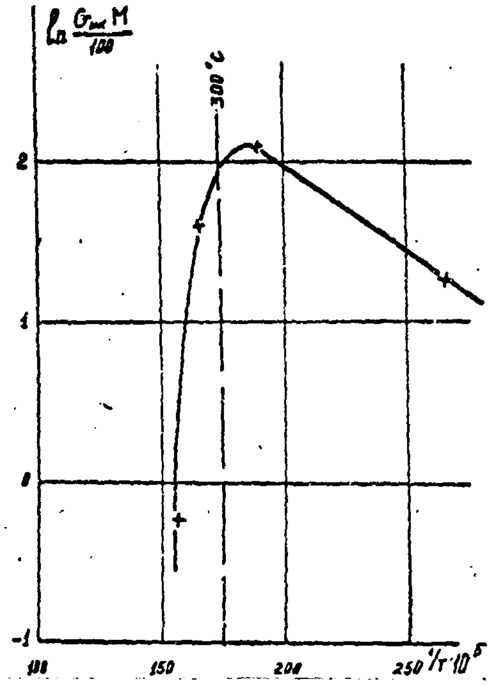

Fig.11. Relation of initial yield of high boiling product in hydrostabilized gas oil to the temperature of radiolysis.

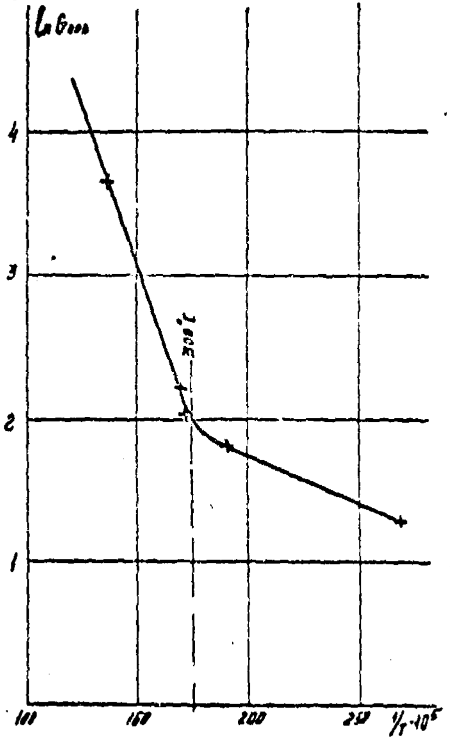

Fig.12. Relation of initial yield of gases in hydrostabilized gas oil to the temperature of radiolysis.

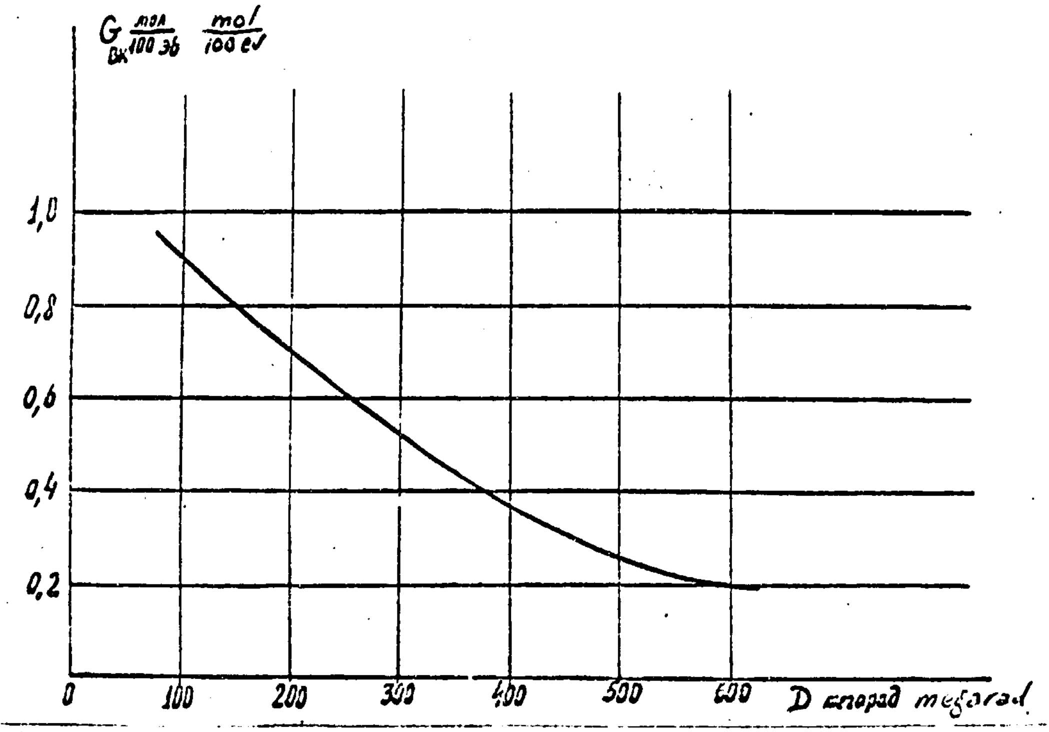

Fig.13. Relation of yield of high boiling product in hydrostabilized gas oil to the irradiation dosage at a radiolysis temperature of 330°C.

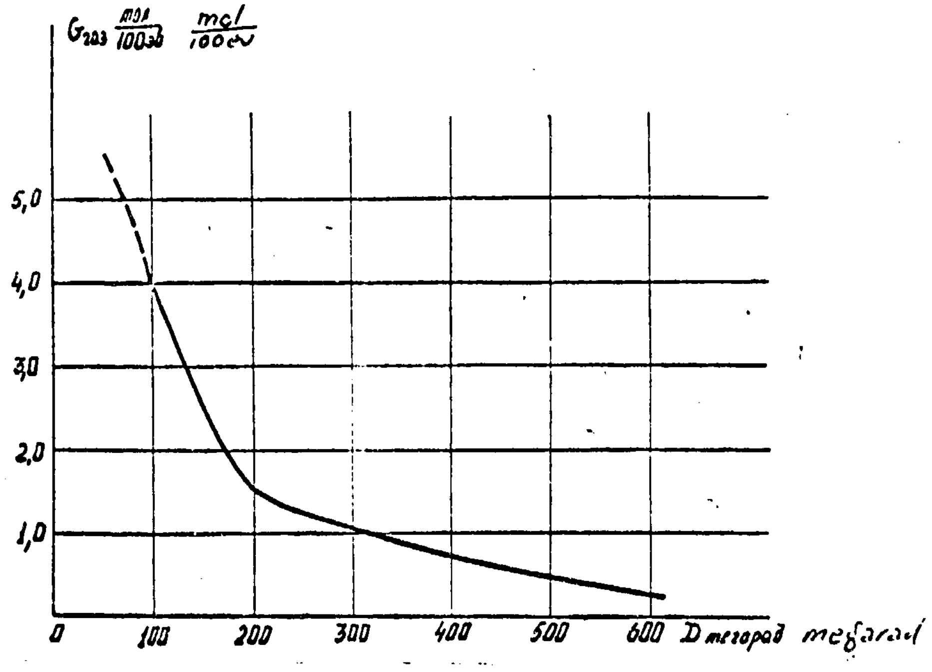

Fig.14. Relation of yield of gases of hydrostabilized gas oil to the irradiation dosage at a radiolysis temperature of 330°C.

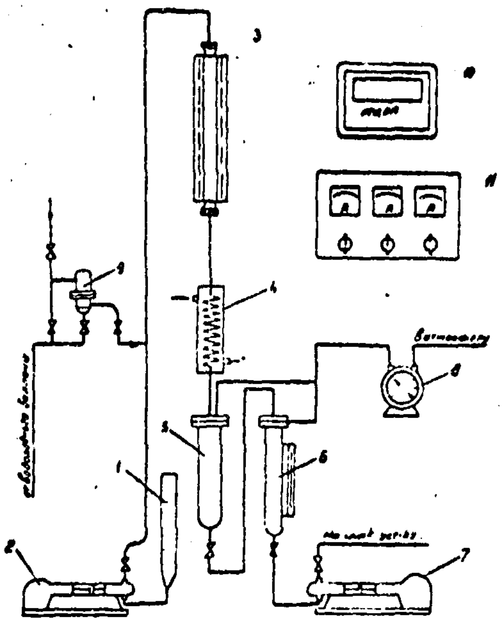

Fig.15. Main scheme of a loop regenerative installation. 1 - Measuring hopper. 2 - Raw product pump. 3 - Reactor. 4 - Comdenser. 5 - High pressure separator. 6 - Low pressure separator. 7 - Feed pump. 8 - Gas meter. 9 - Pressure regulator.

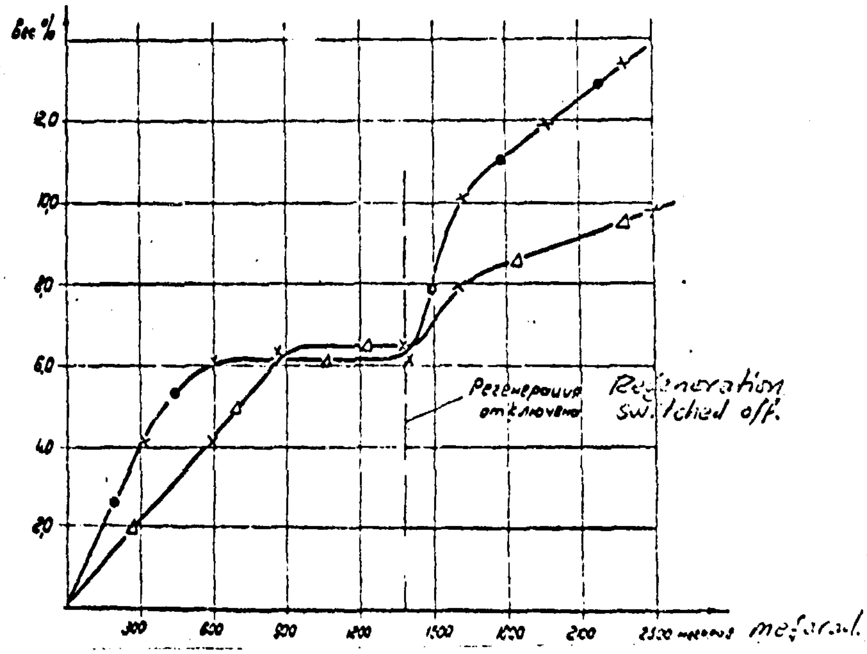

Fig.16. Change of concentration of high boiling product and of unsaturated hydrocarbons in hydrostabilized gas oil in the loop during regeneration.

⊙ - concentration of high boiling product.

▲ - concentration of unsaturated hydrocarbons.

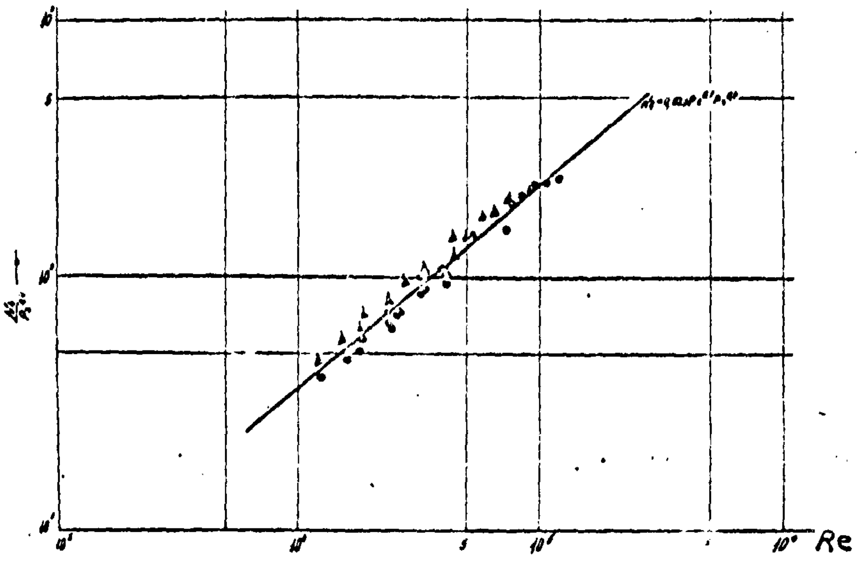

Fig.17. Data processing of measurements - coefficients of heat transfer to monoisopropyldiphenyl and to hydrostabilized gas oil, according to Kraussold formula.

o - monoisopropyldiphenyl.
Δ - hydrostabilized gas oil.

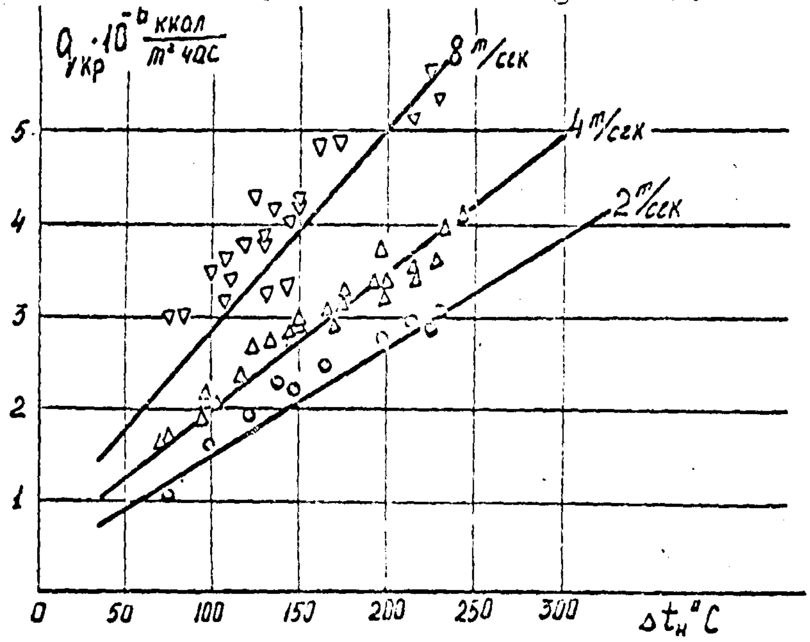

Fig.18. Data processing of measurements of critical thermal loadings during heat transfer to monoisopropyldiphenyl in a cyclic gap, according to the L.E.Mikhaylov formula for a pressure of 5 atmospheres.

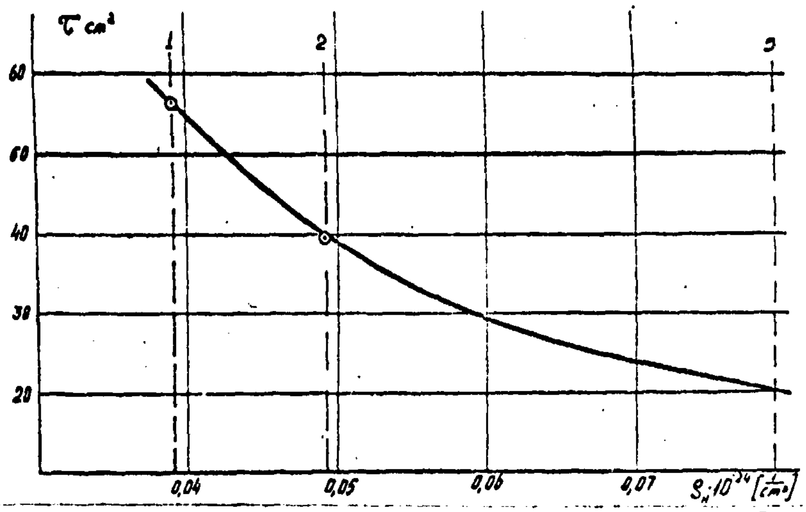

Fig.19. Comparison of measured and calculated values of the square of the length of moderation of neutrons in organic moderators.

1. Diphenyl (according to U.U.Braun).
2. Monoisopropyldiphenyl (according to L.N.Yurova).
3. Hydrostabilized gas oil.

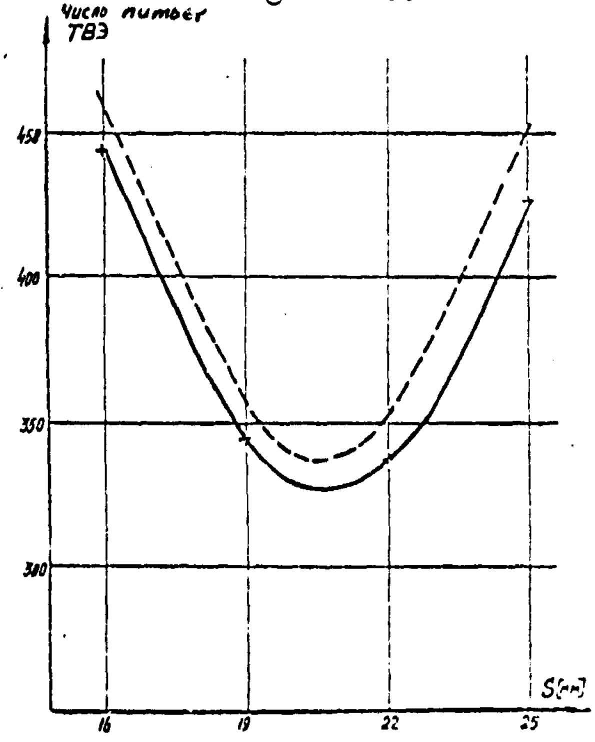

Fig.20. Experimental and calculated ratio of the critical loading to the lattice pitch in experiments with the Energy Coefficient - 10 Fuel Element and moderator - monoisopropyldiphenyl. (Broken curve represents calculated values).

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