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The Effect of Nuclear Irradiation at Ambient Temperatures on the Viscosity and Chemical Structure of a Coal Tar Pitch

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A high temperature coal tar pitch was irradiated up to a dosage of $3{\cdot}5 \times 10^8$ rads in a nuclear reactor. Samples were sealed either under a vacuum or under an atmosphere of air. Four methods were used to evaluate the pitch after irradiation: (1) viscosity measurements, (2) infra-red analysis, (3) X-ray diffraction analysis, and (4) mass spectrometric analysis of the evolved gas. All measurements indicate that the high temperature coal tar pitch underwent negligible changes in its physical and chemical structure.

THE most important process (tonnage-wise) for the conversion of coal into chemicals is high temperature carbonization—destructive distillation with resulting production of coke, tar, light oil and gas. There is interest in finding new and expanded markets for coal tar and coal tar pitch. The main objective of the present study was to obtain information on the stability of a typical high temperature coal tar pitch to nuclear irradiation. Such basic information may lead to the enhanced utilization of pitch as a radiation resistant material.

In a survey programme[1] directed at finding an impervious lining material for radioactive waste basins, the radiation stability of a roofing tar (softening point, 70°C) was previously studied by Bresee and co-workers. Samples subjected to a cobalt-60 source of radiation up to 10^9 roentgens retained their ductility but were hardened with increasing exposure (indicated by an increase in softening temperature). Gases (primarily hydrogen and small amounts of carbon dioxide) were evolved from the tars during irradiation. Irradiated tars showed a slightly honeycombed structure. It was concluded that coal tars were satisfactory insofar as their resistance to radiation was concerned.

In this study, the effect of reactor irradiation (gamma plus neutron) on a high temperature coal tar pitch will be studied using appropriate analytical techniques.

EXPERIMENTAL

Pitch sample used—A commercial high temperature coal tar pitch was chosen for the study. An analysis of the pitch is presented in *Table 1* and miscellaneous properties of the pitch are shown in *Table 2*.

Table 1. Analysis of the pitch

Element	C	H	N	S	*Other*
Concentration, % w/w of pitch	92·05	4·52	0·50	0·54	2·39

Table 2. Miscellaneous properties of the pitch

Coking value, %	44·2	*Insoluble in, %*	
Specific gravity, at 25°C	1·29	*Quinoline*	7·8
Softening point, °C	96·0	*Benzene*	25·2

Preparation of pitch samples for irradiation—The samples were ground to −40 mesh and about 40 g was placed in a quartz container (4 in. long by 1¼ in. i.d.) and sealed under one of the following conditions:

1. Vacuum—the samples were evacuated until the pressure was less than 10 μ of mercury and then sealed.
2. Atmospheric—the samples were sealed in air at atmospheric pressure. (Samples so treated are hereafter referred to as air-irradiated.)

Radiation conditions—The samples to be irradiated were bundled together four at a time, wrapped with a sheet of cadmium (1 mm thick) to decrease activation from thermal neutrons, lowered in a 3 in. i.d. aluminium tube, and positioned at the centre of one face of The Pennsylvania State University Reactor. The reactor is an enriched uranium, water-moderated type capable of operating at a maximum power level of 100 kW. Bundles were exposed to various total dosages[*] ranging from $3{\cdot}5 \times 10^4$ up to $3{\cdot}5 \times 10^8$ rads. An irradiation time of 1000 min was equivalent to the absorption of $3{\cdot}5 \times 10^8$ rads, 100 minutes was equivalent to $3{\cdot}5 \times 10^7$ rads, etc. For the 1000-minute irradiation, with the cadmium shield in place, the following is a summary of the integrated fluxes and energy absorbed by a sample of pitch, as calculated in detail elsewhere[2].

Source	Rads absorbed	Corresponding integrated flux
Direct gamma rays	$2{\cdot}0 \times 10^8$	$2{\cdot}2 \times 10^{17}$ gamma rays/cm^2
Thermal neutrons (Gamma rays from thermal neutron capture)	$1{\cdot}2 \times 10^8$	$5{\cdot}3 \times 10^{16}$ gamma rays/cm^2
Fast neutrons	$0{\cdot}3 \times 10^8$	$4{\cdot}4 \times 10^{16}$ neutrons/cm^2

Gas analysis—Analysis of the gas in the container following irradiation was determined by mass spectrometry.

Viscosity measurements—An apparatus was constructed using the Brookfield Synchrolectric viscometer to determine the viscosity of the pitch before and after irradiation. A pitch container and a special spindle were designed for use with the viscometer motor, permitting 33 g of sample to be tested. For the temperature range (100° to 170°C) over which measurements were made, the difference between the top and bottom temperatures of the container was no more than 0·5°C. The complete operating procedure may be

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[*] The total dosage (in rads) is calculated from the given integrated intensity of radiation (in roentgens) and depends on the properties and dimensions of the system. A detailed procedure for calculating this is presented in A. ROEGER's *M. S. Thesis*[2].

found elsewhere[2]. Error of measurement was ±5 per cent (average) and ±10 per cent (maximum).

Infra-red spectra—The potassium bromide disc technique[3, 4] was used in conjunction with a Perkin–Elmer model 21 double beam recording spectrophotometer. The concentration of pitch in potassium bromide was 0·4 per cent. Variation in duplicate spectra was about 1 to 3 per cent. Detailed procedures may be found elsewhere[2].

X-ray diffraction—An x-ray diffraction pattern was run on a sample of pitch which was irradiated to $3{\cdot}5 \times 10^8$ rads in air. A 164° (2θ) General Electric x-ray diffraction unit, XRD-3, with copper radiation was used. Standard procedures[5] were employed.

RESULTS

Analyses of the gas evolved from the irradiated pitch—Of particular interest were (*1*) the type of evolved gases, (*2*) the total quantity of gas evolved at

Table 3. Analyses of gases evolved from the irradiated pitch (an air- and water-free analysis)

Original atmosphere	$< 10\,\mu$ Hg *air*	$< 10\,\mu$ Hg *air*	*1 atm air*
Dosage (rads)	$3{\cdot}5 \times 10^7$	$3{\cdot}5 \times 10^8$	$3{\cdot}5 \times 10^8$
Estimated pressure in quartz container (mm Hg)	13	31	800
Analysis of evolved gas (% by vol.)			
Hydrogen	51·5	78·0	35·5
Carbon dioxide	39·3	17·8	10·8
Carbon monoxide	7·6	3·0	53·8
Acetylene	0·3	0·5	—
Methane	0·7	0·6	—
Ethane	0·2	0·1	—
Propane	0·3	0·1	—
	99·9	100·1	100·1
Volume of evolved gas (cm^3/g pitch)	0·012	0·028	0·071
Analyses of evolved gas (Moles/g pitch) $\times 10^6$			
Hydrogen	0·278	0·975	1·12
Carbon dioxide	0·212	0·223	0·342
Carbon monoxide	0·0410	0·0375	1·71
Acetylene	0·0016	0·0063	—
Methane	0·0038	0·0075	—
Ethane	0·0011	0·0013	—
Propane	0·0016	0·0013	—
	0·5391	1·2519	3·172
G values (Molecules/100 eV)			
Hydrogen	0·0076	0·0027	0·0032
Carbon oxides	0·0069	0·0007	0·0056
Hydrocarbons	0·0002	0·0001	—
Gas	0·0147	0·0035	0·0088

various dosages, (*3*) the threshold dosage, and (*4*) the effect of the presence of oxygen. Preliminary work on samples irradiated *in vacuo* showed three significant trends: (*1*) hydrogen was first detected at 3·5 × 10^6 rads dosage, (*2*) hydrocarbons were present only in trace amounts at 3·5 × 10^8 rads dosage, and (*3*) an increase in dosage from 3·5 × 10^7 to 3·5 × 10^8 rads increased the evolution of gas by three times to about 0·03 cm^3 (s.t.p.) per gramme of pitch. The results of the gas analyses on selected samples appear in *Table 3*.

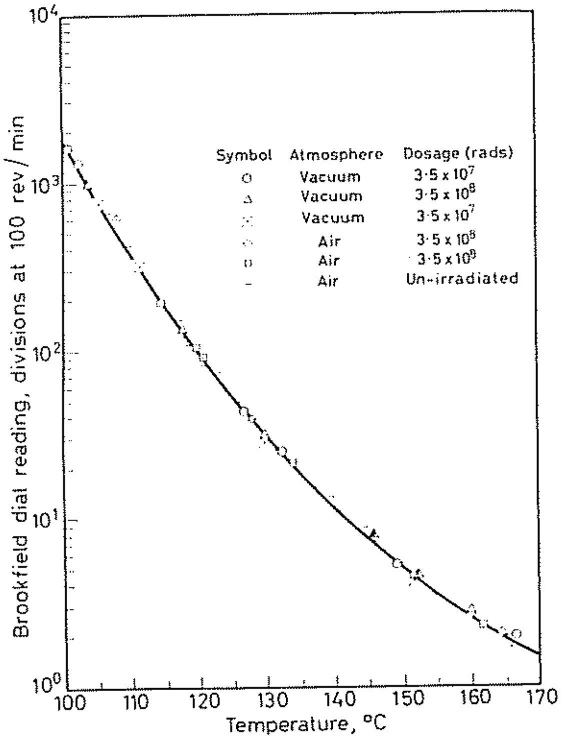

Figure 1. Brookfield dial readings prior to and after irradiation of the pitch

For the samples that were evacuated to less than 10 μ of mercury pressure before sealing and irradiating at 3·5 × 10^7 and 3·5 × 10^8 rads dosage, the hydrogen evolved increased from *ca*. 50 to 80 per cent of the total gas released with increase in dosage. The total hydrocarbon percentage stayed roughly constant while the percentage of carbon oxides decreased markedly. Roughly 85 per cent of the carbon oxides was carbon dioxide for both dosages. On the basis of moles of gaseous product per gramme of pitch, the hydrogen content increased over three times and the acetylene and methane increased substantially upon a tenfold increase in energy absorption. The yields of carbon oxides, on a molar basis, were essentially independent of dosage.

For irradiation to 3·5 × 10^8 rads in 1 atm of air, there was a large increase in the yield of carbon oxides over irradiation in a vacuum to the same dosage. Further, about 64 per cent of the evolved gas was carbon oxides. In marked contrast to the vacuum irradiation, carbon monoxide constituted the majority of the evolved carbon oxides. No hydrocarbons could be detected in the samples irradiated in air because of the dilution effect of the air—less than 10 per cent of the total gas present following irradiation was evolved gas. The moles of hydrogen released per gramme of pitch following irradiation to $3{\cdot}5 \times 10^8$ rads were essentially independent of atmosphere.

The G values for gases, namely the number of molecules of the gas evolved per 100 electron volts absorbed by the pitch, are also presented in *Table 3*, and discussed later.

Viscosity measurements—Newtonian flow properties were exhibited by the pitch over the rates of shearing used in the investigation. This characteristic (that is, the shearing stress varied linearly with the rate of shear) meant that one spindle could be used to measure viscosity over a wide temperature range simply by increasing the spindle speed when small scale readings were being approached. The dial reading was kept at a maximum (for any one speed) to avoid reading errors. When the temperature was raised, the reading would decrease from full scale; and the spindle speed would be increased to bring the reading as near to full scale as practicable. To compare viscosities directly, all readings were adjusted to a spindle speed of 100 rev/min. The Brookfield dial readings were related directly to the viscosity.

Steady-state Brookfield dial readings obtained from runs on the un-irradiated and irradiated pitch are shown graphically in *Figure 1*. Over the

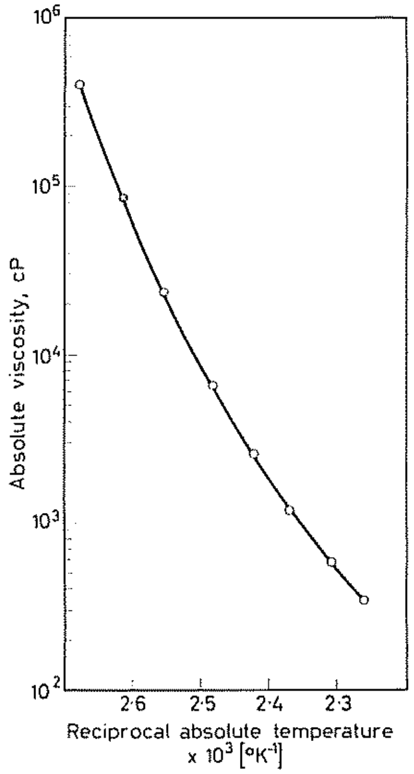

Figure 2. Brookfield viscosity of the un-irradiated pitch as a function of the reciprocal absolute temperature

temperature range 100° to 170°C, the dial readings of the irradiated pitch fell within the limits of reproducibility of the dial readings for the un-irradiated pitch. By applying a calibration factor to the torque reading, an absolute viscosity can be calculated[2, 6]. As suggested by E. N. DA C. ANDRADE[7], the viscosity data for the un-irradiated pitch are plotted in *Figure 2* as log absolute viscosity versus the reciprocal of the absolute temperature. E. W. VOLKMANN[8] discusses reasons for the non-linearity of such a plot with liquids having properties similar to pitch.

Infra-red spectra of irradiated pitch—A representative spectrum of the irradiated pitch (dosage $3{\cdot}5 \times 10^8$ rads, in air) is compared with that of the un-irradiated pitch in *Figure 3*. Ten significant absorption bands characterize the pitch. They are: 3·3 μ (aromatic CH), 3·45 μ (naphthenic and aliphatic CH, CH_2 and CH_3), 6·25 μ (aromatic C=C), 6·95 μ (naphthenic and heterocyclic CH_2), 7·27 μ (aliphatic CH_3), 7·5 μ (aromatic OH), 9·67 μ (aromatic ethers and minerals), and three substituted aromatic absorption bands at 11·4, 12·3 and 13·35 μ. The absorption band at 2·9 μ is undoubtedly primarily a 'potassium bromide artefact', caused by its strong retention of moisture.

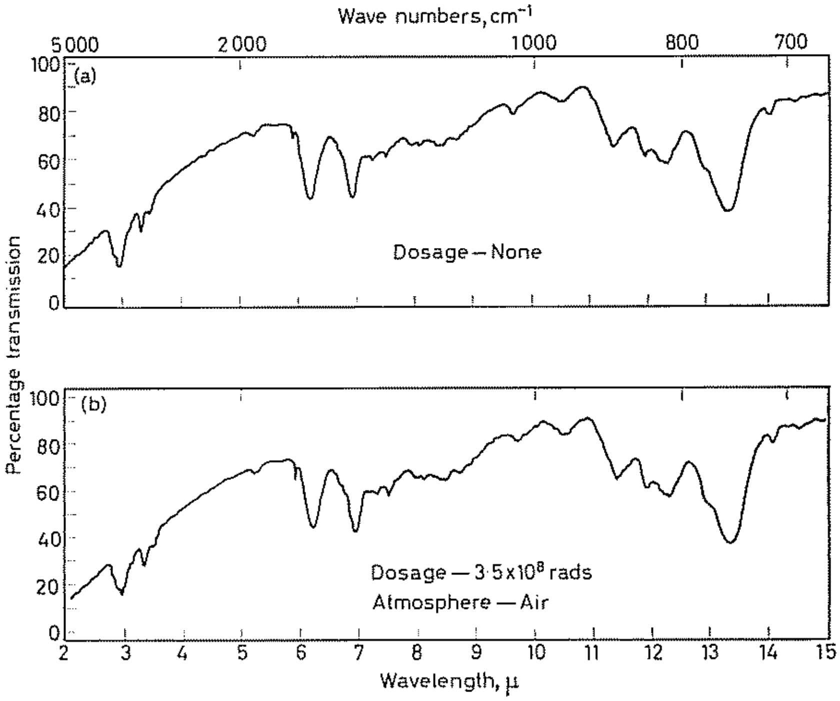

Figure 3. Representative infra-red absorption spectra prior to and after irradiation of the pitch

As is seen, the patterns are very similar. Spectra were obtained on three samples of each pitch and the relative peak heights of the above absorption bands measured. For irradiation to the highest dosage, either in a vacuum or air, significant but small changes in the intensities were found for the 7·27, 11·4 and 12·3 μ bands. The intensity of the 7·27 μ band decreased, whereas the intensities of the 11·4 and 12·3 μ bands increased. No significant changes in intensities were found for the other bands. At lower dosages, no significant changes in intensities were found for any of the bands.

DISCUSSION OF RESULTS

It is apparent from the results that irradiation in air, as compared to irradiation *in vacuo*, increases the production of gaseous carbon oxides. In particular, the yield of carbon monoxide was increased some 40-fold at a radiation dosage of $3{\cdot}5 \times 10^8$ rads. It is clear that the large amount of carbon monoxide was formed primarily from attack of the pitch by one or more active species (produced by irradiation) and not from attack of the evolved hydrocarbon gases. That is, the result of irradiation of the evacuated capsules at $3{\cdot}5 \times 10^8$ rads shows that insufficient hydrocarbons were produced to be the major source of carbon for the carbon monoxide yield in the air-irradiated experiment. N. BACH reported[9] that molecular oxygen was a very efficient acceptor for most organic radicals with the resultant formation of peroxides and other oxidation products. Large amounts of the carbon oxides may be explained by the findings of Bach. In particular, he found that both peroxides (R_1OOR_2, ROOH and H_2O_2) and end products of oxidation were formed; and, at a definite dosage rate, the peroxides began to decompose, liberating methane and carbon dioxide. Upon further irradiation, a steady-state concentration of peroxides was established.

The greater amounts of carbon monoxide evolved from the air-irradiated pitch sample may be explained from the conclusions drawn by P. HARTECK and S. DONDES[10]. They reported that for pile irradiation of atmospheric pressure carbon dioxide containing an inhibitor (1·25 per cent air), G decomposition values were about 7—relatively high. This decomposition resulted in the formation of oxygen and carbon monoxide. In the present work, the oxygen produced may have reacted with the pitch to form still more carbon monoxide. A. O. ALLEN[11] cited a similar example, where carbon monoxide appeared in the product mixture resulting from the irradiation of carbon dioxide.

E. L. COLICHMAN and R. H. J. GERCKE[12] have studied the radiation stability of polyphenyls at elevated temperatures. They found that the gas yields increased with the energy input, the G_{gas} value decreased as the dosage increased, the G_{polymer} value increased as the dosage increased, and the stability decreased as the temperature during radiation was raised. Large percentages of hydrogen and smaller amounts of the simpler hydrocarbons were found. G_{gas} values were about 0·005 at room temperature and G_{polymer} values were about 0·05. The gas yields were about 2 cm^3/g at s.t.p. Except for the effect of temperature on irradiation and the G_{polymer}value, which were not investigated in this research, the trends shown by the polyphenyls are comparable with those of the pitch. However, the gas yields obtained from the pitch were quite small compared with those from the polyphenyls.

A study of the effects of radiation on turbine oils[13] showed that about 0·05 cm^3 of gas was evolved per gramme of oil per 10^6 rads absorbed. This is another comparison which substantiated the idea that the pitch is very stable to pile irradiation because only about 0·03 cm^3 of gas was evolved from the pitch at $3·5 \times 10^8$ rads—about half the evolution of gas for over 350 times the energy absorbed in comparison to the turbine oil. It is possible that the nature of the irradiation and the radiation dosage rates in the two studies differed considerably. Therefore, if the above comparisons are to be meaningful, it has to be assumed that equal absorbed dosages of radiation lead to similar qualitative and quantitative effects regardless of radiation type and/or dosage rate. Several investigators have indicated that this is a reasonable assumption[14, 15].

Not only are the G values extremely low for aromatics, but decomposition is expected to be somewhat lower in the liquid state than in the vapour state. When a bond is broken, the constraints on the movement of the resulting fragments due to the presence of neighbouring molecules in the liquid state will favour recombination of the fragments to reform the original compound. This effect was discussed by J. FRANCK and E. RABINOWITSCH[16] for photochemical reactions and is often called the 'cage effect'. Hence, since pitch is by nature a relatively viscous liquid, the 'cage effect' might be interpreted to mean that a minimum of polymerization and gas evolution would be produced by irradiation, except possibly close to the surface of the pitch.

Viscosity measurements—There generally was better reproducibility of the viscosity measurements at temperatures below 125°C because under these conditions, with an actual spindle speed of 100 rev/min, the dial reading was approaching full scale. Below about 120°C, the actual speed was less than 100 rev/min and the dial readings were usually approaching full scale at each speed from 50 to 2·5 rev/min. Above 125°C, since the 100 rev/min speed was the limit of the viscometer, the dial readings gradually became smaller as the temperature was increased. Brookfield Engineering Laboratories reported[6] that the possible percentage error at 100 per cent of full scale is 1 per cent, whereas at readings of 1 dial division (1 per cent of full scale), the error is 100 per cent.

From these observations on the reproducibility of the dial readings, it is concluded that at the dosages given the samples, the viscosity of the pitch remained unchanged upon irradiation up to $3·5 \times 10^8$ rads either *in vacuo* or in an atmosphere of air. Any polymerization effects that would be detected by differences in viscosity of the pitch fell within the limits of reproducibility of the dial reading/temperature relationship. There was evidence to suspect, however, that some polymerization took place above a dosage of $3·5 \times 10^7$ rads because of the presence of hydrogen and hydrocarbon gases in the gas evolved from the pitch upon irradiation, as was mentioned in the previous section.

Work that has been done on irradiation of hydrocarbon fuels[17, 18] indicated that the viscosity increase by irradiation by less than 5×10^8 roentgens has not been appreciable. This substantiates the results obtained with the Brookfield viscometer, indicating that the viscosity increased less than ten per cent during irradiation dosage of $3{\cdot}5 \times 10^8$ rads.

Infra-red spectra of the irradiated pitch—The decrease in intensity of the $7{\cdot}27\,\mu$ band shows that there has been a decrease in methyl groups as the sample absorbed $3{\cdot}5 \times 10^8$ rads of energy. This is in agreement with the gas analysis which showed that hydrocarbon gases were evolved from the vacuum-irradiated pitch. The increase in absorption for the $11{\cdot}4$ and $12{\cdot}3\,\mu$ bands indicates that a more heavily substituted ring system was developed. This fact supports the inference that the reactive molecular groups, stripped partially of their hydrogen, polymerized to form a more highly condensed structure. The gas analyses showed that significant amounts of hydrogen were evolved from the samples, especially at the higher irradiation dosages.

From this study it appears that infra-red spectroscopy provides a less sensitive indication of change in structure than does gas analysis. Slight changes in the infra-red spectra are noticed after a dosage of $3{\cdot}5 \times 10^8$ rads, whereas mass spectrometric analysis has shown that gases are evolved at as low as $3{\cdot}5 \times 10^6$ rads.

Analyses of pile-irradiated hydrocarbons have been studied by R. H. MOORE[19]. He found that benzene lost 45 per cent and 1,2-benzanthracene, 23 per cent, by weight, of their original material upon irradiation. Although he did not state the dosages received by the aromatics, there was a diminishing extent of destruction with increasing size of the molecule. Thus, since pitch is composed of 3- to 7-ring structures[20] and is very highly aromatic[21], it might be expected that irradiation would have a minimum effect on its decomposition. Various authors[11, 22] state that aromatics exhibit the greatest stability of all organics toward radiation.

X-ray diffraction patterns of the irradiated pitch—An x-ray diffraction pattern on the pitch irradiated in air to $3{\cdot}5 \times 10^8$ rads was compared with that on the un-irradiated pitch. In both cases, the (002) reflection was observed at 23·5° (2θ), giving an interlayer spacing of 3·78 Å. This shows that the two-dimensional carbon structure present in the original pitch did not change significantly during irradiation.

CONCLUSIONS

A high temperature coal tar pitch was found to be very stable towards pile irradiation up to the limits studied (dosage of $3{\cdot}5 \times 10^8$ rads) probably because of its highly aromatic nature. Of the analytical methods used to follow the stability of the pitch to irradiation, analysis of the gas produced was found to be the most sensitive.

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