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ORGANIC COMPOUNDS IN FISSION REACTORS.

I. THE DISPERSION OF ThO_2 IN NONPOLAR SOLVENTS

W. H. Baldwin

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ORGANIC COMPOUNDS IN FISSION REACTORS. I. THE DISPERSION OF ThO_2 IN NONPOLAR SOLVENTS

W. H. Baldwin

ABSTRACT

The advantages of the use of organic liquids in fission reactors to minimize corrosion and pressure problems led to a study of the dispersion of thoria and of the solution of thoria and urania in such fluids. This paper deals with the dispersion of thoria in nonpolar solvents (particularly biphenyl), the settled volume being used to determine the degree of dispersion. Benzoic acid (80 g per kg of ThO_2) and uranyl benzoate were among the successful dispersing agents that were adsorbed from solution. A coating that permitted the dispersion of ThO_2 was formed by treatment with Dri-Film. Further papers in this series will deal with thoria and urania dissolved in biphenyl.

INTRODUCTION

The interest in the use of organic compounds in fission reactors has been extended to the proposal that ThO_2 dispersed in the organic liquid might prove a useful blanket material. Polyphenyl hydrocarbons (*1*) are relatively resistant to radiation; hence aromatic hydrocarbons were used here for laboratory tests on the dispersion of ThO_2. After a few preliminary tests with benzene, biphenyl (bp 254°C) was selected for further testing at elevated temperatures.

The dispersion of oxide-type pigments in nonpolar solvents has been studied by Harkins and co-workers (*2–4*). Their results show that the degree of dispersion was a function of the amount of material adsorbed on the pigment. For our purposes we chose the final settled volume of the oxide as an index of the degree of dispersion that resulted from various treatments.

EXPERIMENTAL PROCEDURE

Preparation of Materials. – The benzene (reagent-grade, thiophene-free material) was used directly. No attempt was made to dry it before use.

The biphenyl (best grade available) was distilled under reduced pressure. The first 10% of the distillate was discarded and the next 40% used. This product was anhydrous, mp 71.5°C, and showed only a single component by vapor chromatography.

Reagent-grade or Eastman white-label-grade additives were employed when available. However, the oleic acid and the benzene sulfonic acid were practical grade.

Uranyl benzoate was prepared by adding an aqueous sodium benzoate solution to an aqueous uranyl nitrate solution until the pH of the mixture reached 5. The yellow precipitate was filtered, washed twice with boiling water, and dried. Analysis showed 46.0% uranium (the theoretical value for $C_{14}H_{10}O_6U$ is 46.5%).

Thorium dioxide samples prepared by thermal decomposition of the oxalate were supplied by McBride (*5*). In addition to the ordinary oxides several modifications were tested (Table 1): thorium dioxide was treated with ethyl silicate and fired to produce a coating of SiO_2 (492A-2); 5 mole % uranium oxide was incorporated in the oxide by coprecipitating the thorium-uranous oxalates and firing the mixture (494A-4); another sample of ThO_2 was treated with Dri-Film to provide an organic coating (Appendix II). All preparations had average particle sizes between 1 and 4 μ.

Equilibration. – The sample of thorium dioxide (5 g air-dried) was placed in a Pyrex tube that

Table 1. Preparation of ThO_2 for Dispersion Tests

Sample No.	Starting Materials	Final Firing Temperature (°C)
ACDC-13	Thorium oxolate	800 (4 hr)
492A-1	Thoria, fired 4 hr at 1000°C	1600 (12 hr)
492A-2	Thoria, fired 24 hr at 650°C, cooled and treated with ethyl orthosilicate	1000 (4 hr)
493A-3	Thoria, fired 24 hr at 650°C	650 (4 hr)
494A-4	5 mole % U in ThO_2, fired 4 hr at 650°C*	800 (24 hr)
LO-29	Thorium oxalate	800 (4 hr)
DF	Thoria, fired 24 hr at 650°C, cooled and treated with Dri-Film	150

*Coprecipitated as thorium-uranous oxalates and fired.

had been sealed and flattened at one end (0.9 cm ID × 30 cm high). The tube and its contents were heated in an oven at 145°C for more than 20 hr. The necessary amount of dispersing agent was added, followed by melted biphenyl (10 g). The tube and its contents were evacuated to 0.1 mm Hg and degassed by a combination of melting and freezing. The tube was then sealed at this reduced pressure.

The sealed tubes were placed horizontally in the oven (145°C) for 16 hr for equilibration (with occasional agitation). The tubes were again shaken and placed vertically in the oven for settling (16 hr). The height of the settled column was measured and the volume calculated for 1 g of ThO_2. The above procedures of equilibrating and settling were repeated until the settled volume was constant. Usually three such successive treatments were sufficient. Deviations from the general procedure will be noted when the experiments are discussed later.

DISCUSSION

Dispersion in Benzene. – The dispersion tests that were run in benzene (at 24°C) were undoubtedly influenced by the presence of water (in the benzene and adsorbed on the ThO_2). However, qualitative differences were noted in the settled volumes obtained with various additives (Table 2).

The ThO_2 was better dispersed in water than in benzene (settled volume 0.68 ml per g of ThO_2 as against 0.96). The suspension of ThO_2 in benzene showed gross agglomeration that was immediately dispersed by the addition of oleic acid and by shaking. The same settled volume resulted from the addition of the oleic acid along with the benzene. Both benzoic and oleic acids were effective dispersing agents for ThO_2 in benzene.

Oleic acid was beneficial in dispersing all the ThO_2 preparations, but differences were noted in the degree of effectiveness. The thorium-uranium oxide (sample 494A-4) was as effectively dispersed as the ThO_2 that was treated similarly (sample 494A-3), but neither sample was so effectively dispersed as some of the other samples (ACDC-13).

Dispersion in Molten Biphenyl. – Several polar compounds were tested for their dispersing action in molten biphenyl (see Table 3). The long-chain carboxylic acid (stearic) gave good dispersions. Both benzoic and benzene sulfonic acids were just as effective. Some hydroxyl compounds (myristyl alcohol and *p*-hydroxybiphenyl) were effective dispersing agents, while benzhydrol was less effective. The sulfur analog of 2-naphthol (2-naphthalenethiol) had less effect than *p*-hydroxybiphenyl. Significantly, dispersion was also produced by a metallic salt, uranyl

Table 2. Settled Volume of ThO_2 in Benzene

Sample No.	Additive	Concentration (mg per g of ThO_2)	Settled Volume (ml per g of ThO_2)
ACDC-13	None		0.96[a]
	Oleic acid	100	0.40[b] 0.40[c]
	Benzoic acid	100	0.51
492A-1	Oleic acid	100	0.37
492A-2	Oleic acid	100	0.44
493A-3	Oleic acid	100	0.54
494A-4	Oleic acid	100	0.53
	Benzoic acid	20	0.70

[a]In water instead of benzene the settled volume was 0.68 ml per g of ThO_2.
[b]Oleic acid added to ThO_2 followed by benzene.
[c]ThO_2 shaken with benzene, allowed to stand 16 hr; oleic acid added, shaken and allowed to stand 16 hr.

Table 3. Effect of Additives on the Settled Volume* of ThO_2 in Biphenyl

Additive	Concentration (mg per g of ThO_2)**	Settled Volume (ml per g of ThO_2)
Benzene sulfonic acid	15	0.44
Stearic acid	24	0.43
Glutaric acid	13	0.55
p-Hydroxybiphenyl	17	0.43
p,p'-Dihydroxybiphenyl	18	0.79
2-Napthalenethiol	16	0.86
Benzhydrol	18	0.91
Myristyl alcohol	22	0.43
p-Nitrobiphenyl	20	0.65
Uranyl dibenzoate	84	0.50
Benzoic acid	10–12	0.46, 0.42, 0.46, 0.42, 0.40

*Sample LO-29, from fired thorium oxalate.
**Approximately 0.1 formula weight per kg of ThO_2.

benzoate, which, while having a low solubility in molten biphenyl, showed effective dispersion.

The bifunctional compounds included in this series were less effective dispersing agents than the monofunctional compounds. Hydroxybiphenyl was better than dihydroxybiphenyl (0.43 ml as against 0.79 ml per g of ThO_2), and stearic acid was better than glutaric acid (0.43 ml per g of ThO_2 compared with 0.55).

The amount of benzoic acid added affects the settled volume (Fig. 1). A 20–30% difference in the settled volume (0.46 ml as against 0.38 ml per g of ThO_2) was noted between 10 mg of benzoic acid per g of ThO_2 and ten times as much benzoic acid. However, with less benzoic acid the settled volume was considerably larger.

In addition to its effect on the settled volume the dispersing agent (benzoic acid) reduced the rate of settling (Fig. 2).

Water in the mixture of ThO_2, biphenyl, and benzoic acid had little effect upon the settled volume (Table 4). In test 3 (20 mg of H_2O per g of ThO_2) visible drops of water appeared in the free space above the mixture after it had cooled to room temperature. It seems likely that at 145°C the benzoic acid was preferentially adsorbed on the ThO_2 and that the H_2O was displaced into the atmosphere over the mixture. At room temperature, Harkins *et al.* (*2–4*) found a pronounced interference from water.

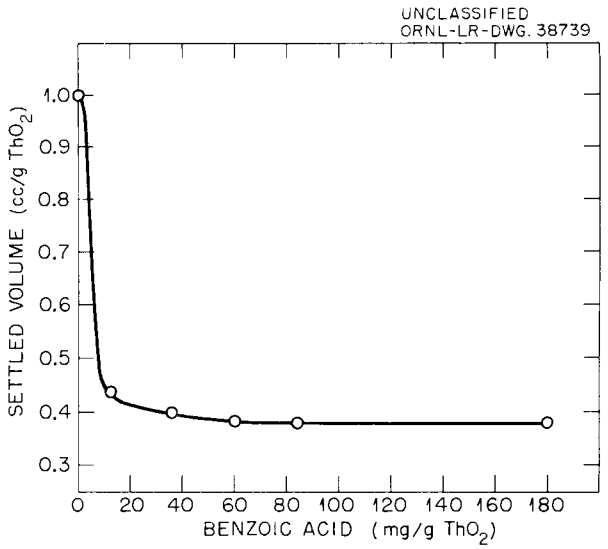

Fig. 1. Effect of Benzoic Acid on Settled Volume of ThO_2 Dispersed in Biphenyl (145°C).

The coating of the thoria surface with Dri-Film was also effective in reducing the settled volume of the oxide (see Table 5 and Appendix II). Heat (42 hr at 255°C) had a slightly deleterious effect upon the settled volume.

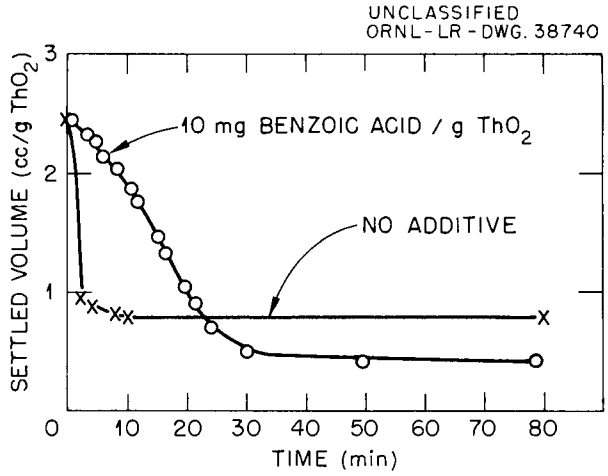

Fig. 2. Settling Rate of ThO_2 Dispersed in Biphenyl (145°C).

Table 4. Settled Volume* of ThO_2, Dispersed with Benzoic Acid (10 mg per g of ThO_2) in Biphenyl

Test No.	Treatment	Settled Volume (ml per g of ThO_2)
1	Mixture heated under reduced pressure to dehydrate	0.40
2	Air-dried ThO_2; not heated	0.42
3	Air-dried ThO_2; 20 mg of H_2O per g of ThO_2 added to mixture	0.42

*Sample LO-29, from fired thorium oxalate.

Table 5. Settled Volume of Dri-Film–Treated ThO_2

Solvent	Temperature of Settling (°C)	Settled Volume (ml per g of ThO_2)
Benzene	24 ± 1	0.75
Biphenyl	145 ± 3 (160 hr)	0.57
	145 ± 3 (42 hr at 255°C)	0.62

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The timely suggestions of E. H. Taylor, E. Guth, and J. P. McBride are responsible for many of the successful features encountered during the survey reported here.

Appendix I

ORGANIC COMPOUNDS USED IN TESTS OF ThO_2 DISPERSION

Name	Simplified Structure	Molecular Weight
Benzene	C_6H_6	78
Oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	282
Benzoic acid	C_6H_5COOH	122
Biphenyl	$C_6H_5C_6H_5$	154
Benzene sulfonic acid	$C_6H_5SO_3H$	158
Stearic acid	$CH_3(CH_2)_{16}COOH$	284
Glutaric acid	$HOOC(CH_2)_3COOH$	132
p-Hydroxybiphenyl	$C_6H_5C_6H_4OH$	170
p,p'-Dihydroxybiphenyl	$HOC_6H_4C_6H_4OH$	186
2-Naphthalenethiol	$C_{10}H_7SH$	160
Benzhydrol	$C_6H_5CHOHC_6H_5$	184
Myristyl alcohol	$CH_3(CH_2)_{12}CH_2OH$	214
p-Nitrobiphenyl	$C_6H_5C_6H_4NO_2$	199
Uranyl benzoate	$(C_6H_5COO)_2UO_2$	512

Appendix II

DRI-FILM CHEMISTRY

General Electric Dri-Film SC-77 is a 50-50 mixture of dimethyldichlorosilane and methyltrichlorosilane, a clear liquid with a boiling point of 66–70°C. It is applied by simply equilibrating the oxide with the vapors at room temperature. The Dri-Film reacts chemically with the water adsorbed as hydroxyl groups on the thoria surface, releasing HCl. Subsequent heating of the oxide (110°C) drives off most of the HCl and forms an organopolysiloxane polymer, bound by silicon-oxygen linkages to the thoria surface by the splitting out of water between hydroxyl groups:

$$CH_3SiCl_3 + 3H_2O \longrightarrow CH_3Si(OH)_3 + 3HCl$$
$$\xrightarrow{\Delta} CH_3SiO{\cdot}OH \text{ (polymer)} + H_2O$$
$$\xrightarrow{\Delta} CH_3SiO_{1.5} \text{ (polymer)} + H_2O$$

Thorium oxide treated with the Dri-Film vapors is not wet by water. Hydrocarbon solvents do not dissolve or remove the film. For a more general discussion see ref 6.

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