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CENTRAL FILES NUMBER

57-1-28

COPY NO. 107

DATE: January 9, 1957

SUBJECT: The HRT Refrigerating System

TO: Distribution

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The HRT refrigeration system, originally employed for the HRE, was designed to use Freon-11, CCl_3F , as the refrigerant material in the secondary loop. A van de Graaff irradiation of this material, reported by Silverman, Heston and Rudolph¹, indicated that serious corrosion problems were probable if Freon were used in the proposed metal system. It was recommended that other materials be considered, especially those which form non-corrosive decomposition products.

In subsequent conversations with R. B. Briggs, ethanol and methanol were suggested for this purpose because some experience with ethanol under irradiation² was available from the Army irradiation center at Dugway, Utah and considerable radiation data on a large number of alcohols had been reported in the literature³. In further conversations Robertson and McLain stated that either ethanol or methanol, because of its low flash point, would constitute a fire and explosion hazard and would therefore be considered unsatisfactory. They indicated that a material possessing a flash point $\geq 140^\circ\text{F}$ was desired.

It became apparent that the following criteria would have to be considered in selecting a refrigerant for the already installed refrigeration system:

(1) The refrigerant should have a suitably low freezing point, $< -40^\circ\text{F}$;
(2) it should be safe both from a toxic and explosion hazard standpoint, i.e., flash point $\geq 140^\circ\text{F}$; (3) it should not form corrosive decomposition products under irradiation; and (4) the refrigerant and its decomposition products should not have a viscosity greater than 40 centipoise at -40°F , so that heat transfer and pumping problems will not be encountered.

Rudolph suggested that ethyl cellosolve, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5\text{OH}$, be considered for use as the HRT refrigerant, although he indicated that the effect of irradiation on such a compound was unknown and should be ascertained. Lundin⁴ requested

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such a determination while stating that cellosolve would be a compromise on several of the above requirements: It has a freezing temperature of -94°F and is considered non-corrosive and relatively non-toxic, but it has a flash point of 104°F (closed cup) and its viscosity (unirradiated) is about 20 centipoise at -40°F .

The writer would like to emphasize here that the above refrigerant criteria make it difficult to choose any single organic compound for this refrigerating system. Materials which have suitably low-freezing points (e.g., alcohols, ethers, ketones and aliphatic hydrocarbons) usually possess low flash points and vice versa; several compounds which are suitable on both these criteria are too viscous for use at -40°F .

A literature study revealed that a much used project compound, tributyl phosphate (TBP), appeared to satisfy several of the necessary requirements. It freezes below -112°F , is relatively non-toxic, and has a flash point of 290°F (open cup). Its viscosity is 3.5 cp at room temperature and 38 cp at -40°F .⁵ Furthermore, its relative stability under irradiation had been reported by Burr⁶. It was noted that the major decomposition product under irradiation is dibutyl phosphate, which possesses a much higher viscosity than TBP (15-fold greater at room temperature). Accordingly, a synthetic mixture* approximating an irradiated sample of TBP was prepared and its viscosity at -40°F determined; a value of 54 cp was obtained, too high for the intended purpose.

It was reasoned that a lower homologous compound might satisfy the viscosity requirements and still possess, to a large degree, the other satisfactory properties of TBP. Such a compound was found in triethyl phosphate (TEP), available from Eastman at about 40 cents per lb. (sp. gr. 1.07). This material has a flash point of approximately 225°F and a viscosity of 7.9 cp (unirradiated) at

* I am indebted to W. H. Baldwin and C. E. Higgins for supplying pure samples of TBP, DBP and TEP and for the use of their distillation apparatus.

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-40°F. Tests on this material are described below in the Experimental Section of this report.

C. E. Winters⁷ has suggested using kerosene or AMSCO as the HRT secondary refrigerant. Kerosene is listed in Lange⁸ as fuel oil No. 1, flash point 100 - 165°F (closed cup). Its freezing point and flash point vary, of course, with the temperature range and composition of the distillate cut. It contains largely saturated hydrocarbons in the C-9 to C-13 range. Since radiation data obtained on pure hydrocarbons^{9, 10} does indicate some "polymer" formation, it is not recommended that kerosene, a material of variable composition, be employed in the HRT refrigeration system.

AMSCO diluents similar to those used in the solvent extraction processes at ORNL, have also been examined. AMSCO 125-82 (odorless mineral spirits), the best grade yet employed, consists of 99% saturated branched chain hydrocarbons, largely polymerized butenes and pentenes, and 1% unsaturates, mainly olefins. The carbon compounds present are largely in the C-8 to C-12 range. The material has a flash point of 128°F.

The statement⁷ "They do have a demonstrated radiation resistance to what I believe would be considerably in excess of your requirements" is in error. AMSCO diluents have not been exposed to the radiation level expected for the HRT refrigerant. The solvent (30% TBP in AMSCO) used in the Thorex process is exposed to 0.01 - 0.02 μ watt hr/liter in one pass through the column. Some samples of solvent have been used for as many as 200 cycles (with an NaOH wash between cycles), mainly to eliminate the hydrolysis product of TBP, dibutyl phosphate.

The HRT refrigerant will be exposed to a dose level of about 4×10^{22} ev/ml; 5 watt hr/l is equivalent to a dose level of only 1×10^{20} ev/ml. Flanary and Goode¹¹ have irradiated AMSCO 125-82 samples in a Co-60 γ source and have

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shown that the production of unsaturates in AMSCO (Iodine No. determination) is linear with dose in the range of 11 to 68 watt hr/l, the latter equivalent to 1.5×10^{21} ev/ml. More recently they have irradiated¹² AMSCO samples to a dose level of 477 watt hr/l or 1×10^{22} ev/ml. In Table I these Iodine No. determinations are summarized.

TABLE I

PRODUCTION OF UNSATURATES IN IRRADIATED AMSCO
125-82

Radiation Dose		Iodine No.
watt hr/ml	ev/ml	
0	0	2.40
11.4		2.65
22.7		3.10
45.4		4.12
68.2	1.5×10^{21}	4.85
477	1.0×10^{22}	9.7
1920*	3.7×10^{22}	12.6

* Iodine No. determined by Flanary and Goode on sample irradiated in van de Graaff by this writer.

G values for the polymerization of olefins of 14 to 2000 have been reported⁹, hence the presence of unsaturates in a high radiation field is a matter of some concern. For this reason and others enumerated above, a sample of AMSCO 125-82 was exposed, as described below, to a radiation level comparable to that expected for the HRT refrigerant.

EXPERIMENTAL

A 30 ml sample of TEP, cooled to 18°C in an apparatus previously described¹, was irradiated to a level of 3.7×10^{22} ev/ml by an electron beam supplied by a van de Graaff generator. (The HRT refrigerant will be exposed to 4×10^{22} ev/ml in the cold traps if used for the full two years' operation). The product gases were not examined, although the type and amounts would be similar to those

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reported by Burr⁶. The viscosity of the irradiated TEP was found to be 27 cp. Potentiometric titration was performed to measure the acidity caused by the presence of diethyl and monoethyl phosphate in the irradiated TEP. The amount of polymeric material obtained was determined as follows:

Weighed samples of the irradiated TEP were neutralized with NaOH, then extracted with ether to leave behind the aqueous soluble diethyl and monoethyl esters. After ether evaporation, the extracted TEP was distilled at 56° at a pressure of 1 mm. A pale yellow viscous liquid residue, non-volatile under these conditions, is designated as "polymer." The infra red spectra of the irradiated TEP was found to be nearly identical with the spectrum of unirradiated TEP, which implies that no unsaturation is introduced into TEP or into any of its non-volatile radiolysis products. The data are summarized below in Tables II and III.

TABLE II

PHYSICAL PROPERTIES OF SUGGESTED HRT REFRIGERANTS

Material	Freezing Pt. ⁸ °F	Flash Pt. ⁸ °F	Viscosity ⁵			
			Room Temp.		-40°F	
			Pure	Irradiated	Pure	Irradiated
Ethanol	-178°	55°				
Methanol	-144°	54°				
Ethyl Cellosolve	-94°	104°			20	
TBP	< -112°	295°	3.5	4.3	38	54*
TEP	-70°	225°	1.6	3.2	7.9	27
AMSCO 125-82	< -55°	128°	1.4	1.5	8.2	12.5

* Synthetic mixture (to simulate irradiation decomposition) of TBP and DBP.

In a similar manner, a 30 ml sample of AMSCO 125-82 was irradiated to 3.7×10^{22} ev/ml in the same apparatus. Again the product gases were not examined, al-

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though they probably consisted largely of hydrogen, and small amounts of alkanes and alkenes. The major portion of the irradiated AMSCO distilled at 63° - 82° at a pressure of 16 mm, the distillation cut of the unirradiated sample. The amount of "polymer" was the dark yellow viscous residue non-volatile under these conditions. The data obtained on AMSCO 125-82, along with those of TEP, are given in Tables II and III.

TABLE III
RADIOLYSIS OF TRIETHYL PHOSPHATE (TEP) AND AMSCO 125-82

	TEP		AMSCO	
		Wt. %		Wt. %
Radiation Time, min.	120		130	
Energy absorbed, ev/ml	3.7×10^{22}		3.7×10^{22}	
Yield ^(a) of DEP	1.8	12	---	
Yield of MEP	0.22	1.5	---	
Polymer Formed		9.5		15.6 ^(b)
Gases, Light Fractions ^(c)		6.8		7.2
Distillate ^(d)		69.5		77.3

(a) Molecules per 100 ev absorbed (G value).

(b) A blank run on unirradiated AMSCO gave 2.5% residue.

(c) By difference

(d) Material which still distills at predetermined temperature and pressure.

From the physical properties and irradiation data presented, it appears that either TEP or AMSCO 125-82 may be satisfactorily employed as the HRT secondary refrigerant. Triethyl phosphate has the higher flash point but also possesses the greater viscosity. Both of these materials appear to be reasonably

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stable to the γ -radiation levels expected. However, it is recommended that whichever refrigerant is employed should be replaced periodically with fresh material.

Recently a detailed examination¹² of the freeze plugs and lines tied into the refrigerating system has revealed that refrigerant tubing is in contact with process lines (especially in the chemical processing cell) whose internal temperature will be as high as 572°F. The irradiations on TEP and AMSCO 125-82 were performed at room temperature; a decided increase in the G values for decomposition may be expected¹³ in going from room temperature to 572°F. Moreover, the life of these materials will be shortened appreciably by pyrolysis at the elevated temperature.

It would be advisable, therefore, to replace the refrigerant after any appreciable exposure to this temperature, especially under radiation. In addition, the lines should be flushed out with fresh refrigerant to dissolve and remove any "polymer" formed. The formation of solid polymeric material is a distinct possibility even if these precautions are observed.

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