SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

LEVEL ARO 17086.1-C

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER DRXRO-PP-L-17086-A-C	2. GOVT ACCESSION NO. AD-A093848
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) Fluoro-Epoxies as Grinding Aids and Water-Resistant Coupling Agents for Ultrafine Ammonium Perchlorate Powders	5. TYPE OF REPORT & PERIOD COVERED
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Frederick M. Fowkes	8. CONTRACT OR GRANT NUMBER(s) DAAG29-79-C-0207
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry, Lehigh University Bethlehem, PA 18015	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709	12. REPORT DATE 22 December 80 13. NUMBER OF PAGES 6
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) MIRADCOM Propulsion Directorate Redstone Arsenal	15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

DTIC ELECTE JAN 13 1981 S E D

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Water proofant for propellant oxidizer
Fluoro-epoxy coupling and grinding agent

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Highly fluorinated epoxy resins, cured with silicone diamines, have been adsorbed from Freon liquids onto ammonium sulfate (a model for ammonium perchlorate) and cured in place as cross-linked monolayers which can be bonded into the urethane rubber matrix. These materials are found to be excellent grinding aids, allowing a ten-fold reduction in particle size compared to present grinding aids. The stability of surface area when stored in humidity chambers was not bad; two batches stored at 51% relative humidity

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

AD A093848

DDC FILE COPY

205460

81 1 12 087

for six weeks retained 30 square meters per gram with a coating of 2.2 mg/m^2, or 1.5 monolayers.

Problem Studied

Missile propellants are fast-burning dispersions of ammonium perchlorate (AP) in an organic binder. Some of these dispersions are made with finely ground AP with average particle diameters less than one micron. The burning rate of these ultrafine AP propellants is quite dependent on the specific surface area of the AP. At the MIRADCOM Propulsion Directorate of Redstone Arsenal accurate specific surface areas of "ultra-fine" AP have been measured and it has been determined that humidity can cause a rapid reduction in the specific surface area of the AP. This effect is considered responsible for the significant decrease in burning rate (and thrust) of such propellants upon storage under humid conditions.

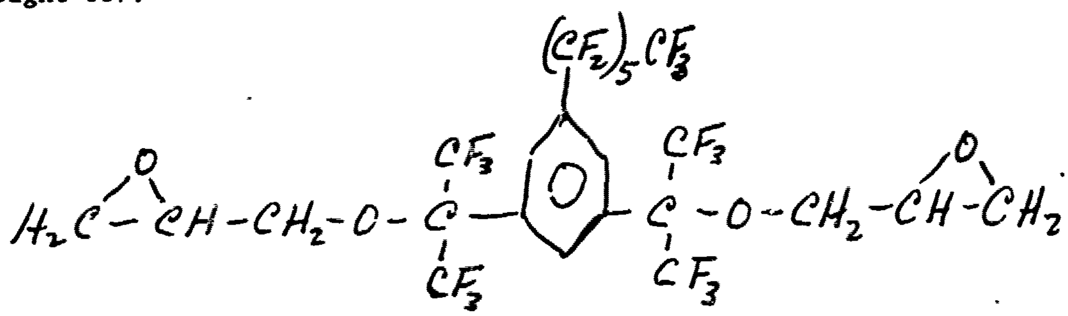
We have studied the use of a novel water-repellant grinding aid, introduced at the time of grinding ammonium perchlorate to the ultrafine state. This grinding aid is the highly fluorinated epoxy system developed by J. R. Griffith of the Naval Research Laboratory.[1-3] It is soluble in the Freon liquid now in use for grinding ammonium perchlorate, adsorbs and polymerizes the surface of the particles, aids in grinding, and forms a cross-linked adsorbed monolayer which has enough alcohol groups to be bonded into the urethane rubber matrix.

We have tested the coated ultra fine powders for their sensitivity to moisture by storing the powders in dessicators with controlled humidity (35%, 51%, and 79% R.H.), and by measuring their specific surface acids with argon adsorption, using the BET method.[4]

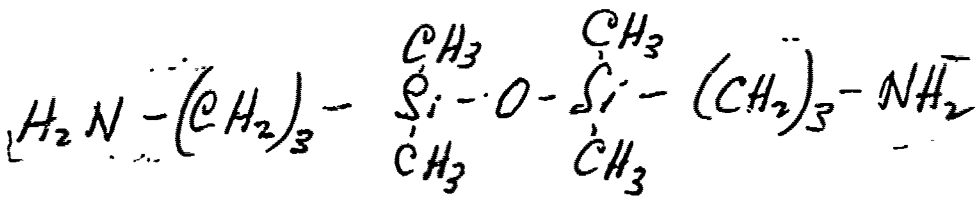
Experimental Details

Additives.

The fluoro-epoxy used in this work is the NRL "C-6" diepoxide of mole weight 837:

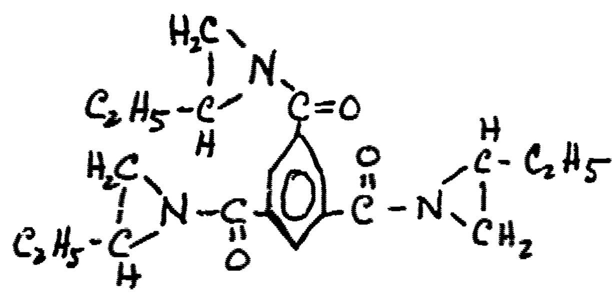


which was polymerized with a silicone diamine (bis γ-aminopropyl tetramethyl disiloxane from Bergstrom Associates in Cincinnatti, Ohio):



The amine and epoxy form a cloudy solution in Freon 112, but on heating five minutes at 50°C. the solution becomes clear as the prepolymer forms.

Since the current process at Redstone Arsenal involves using 3M's aziridine HX-868 as a grinding aid, we used it in our process, also.



Molecular models indicate the aziridine occupies 135 Å^2 per molecule while the epoxy and silicone occupy about 100 Å^2 per molecule, when specific groups are all in contact with the surface. It is expected that the aziridine and amine will react quickly and adsorb on the salt surface with the fluoro-epoxy in contact with the Freon. A complete monolayer of fluoroepoxy (at 100 Å^2 per molecule) will require 1.4 mg per square meter of salt surface.

Milling Procedure. Ammonium sulfate was used as a safe substitute for ammonium sulfate was used as a safe substitute for ammonium perchlorate, and each batch of 5 g of salt was ground in 55 ml of 1,1,2-trichloro-1,2,-trifluoroethane, either at 25°C. in an oven at 50°C. The jar and cylindrical grinding media were of a ceramic material, and the 8.5 cm diameter jar was rolled at 150 rpm.

Results

Quite a few batchs were made, but data on the 24 more significant batches are shown in Table 1. Variations in amounts of additives, in milling time and temperature, and in storage times and humidity were explored. The surface areas were determined on all of these batches, using argon adsorption and the BET method.

The fluoro-epoxy system is shown to be an excellent grinding aid, providing surface areas of 50 square meters per gram, and usually allowing the powder to grind down until only one monolayer of fluoro-epoxy is left (1.4 mg/m^2).

In some batches good resistance to loss of surface during exposure to humidity was abserved, especially in batches 18-24. Poorer resistance was observed when the time or temperature allowed for epoxy polymerization was insufficient. Milling at room temperature for several hours was successful, but only 15 minutes was disastrous, and 120 minutes much better. Milling at 50°C.

was sometimes better than at room temperature.

The weight ratio of epoxy to amine turned out to be quite important. The exact stoichiometric weight ratio (two diepoxide for each diamine) was 6, but better results were obtained when there was excess amine (weight ratios of 3.6 or 3.8). The excess amine can help in adsorption, and might be necessary because of reaction with the aziridine.

Recommendations

1. The fluoroepoxy system is an excellent grinding aid. The aziridine may not be needed.

2. Excess amine appears desirable to promote better properties. It probably assists in the adsorption.

3. Grinding times and temperatures after epoxy addition should be so chosen that the polymerization is complete and so that only a monolayer of the fluoroepoxy results.

4. If there is interest in this process, the next stop, binding of the epoxy into the urethane system, needs to be tested.

Publications

None of this work has been published, and there are no plans to do so at present.

Personnel

The experimental work has been done be two graduate students, Yale West and Joseph Sohara. Mr. Sohara has completed most of his M. S. degree studies on this project.

TABLE I. SURFACE AREAS OF AMMONIUM SULFATE POWDERS STORED IN HUMID ATMOSPHERE AT 23°C.

Batch	Additives				Milling Conditions		Storage Conditions		BET Results			Mg Epoxy
No.	%HX-868	%Epoxy	%Amine	Ratio	Time	Temp	Time	%RH.	M^2/g	C	Reliability	M^2
1	0.2	0	0		15 min	RT	one week	51%	3.4	9.7	Good	0
2	0.2	0	0		15 min	RT	one week	79%	1.4		Poor	0
3	1.2	0	0		120 min	RT	none	-	11.3	25	Excellent	0
4	1.2	0	0		120 min	RT	3 weeks	51%	7.3	61	Good	0
5	1.2	2.4	0.4	6	120 min	RT	none	-	17.9	8.4	Excellent	1.3
6	1.2	2.4	0.4	6	120 min	RT	2.5 weeks	51%	12.6	9.3	Excellent	1.9
7	1.2	2.4	0.4	6	120 min	RT	3 weeks	51%	15.0	10	Excellent	1.6
8	1.2	2.4	0.4	6	120 min	RT	5 weeks	51%	4.3	48	Fair	5.6
9	1.3	1.6	0.4	4	120 min	50°C.	none	-	8.9	12.9	V. Good	1.8
10	1.3	1.6	0.4	4	120 min	50°C.	2 weeks	51%	6.3	37	V. Good	2.5
11	1.3	1.6	0.4	4	120 min	50°C.	3.5 weeks	51%	6.6	13.5	Good	2.4
12	0.6	1.2	0.2	6	15 min	RT	2 weeks	35%	1.6	16	Poor	7.5
13	0.6	1.2	0.2	6	15 min	RT	2 weeks	51%	1.1	22	Poor	10.9
14	0.6	1.2	0.2	6	15 min	RT	2 weeks	79%	1.0	8	V. Poor	12.0
15	2.3	6.3	1.2	5.2	60 min	50°C.	4 weeks	35%	17.9	14	Excellent	3.5
16	2.3	6.3	1.2	5.2	60 min	50°C.	5 weeks	51%	15.0	12.7	Excellent	4.2
17	2.3	6.3	1.2	5.2	60 min	50°C.	3 weeks	79%	11.3	8.5	Poor to fair	5.6
18	0.2	7.5	2.1	3.6	24 hours	RT	5 weeks	35%	53.3	12.3	Excellent	1.4
19	0.2	7.5	2.1	3.6	24 hours	RT	6 weeks	51%	42.6	9.7	Excellent	1.8
20	0.2	7.5	2.1	3.6	24 hours	RT	5 weeks	79%	14.6	183	Fair	5.1
21	0.4	7.1	1.9	3.8	48 hours	RT	6 weeks	35%	47.7	20	Good	1.5
22	0.4	7.1	1.9	3.8	48 hours	RT	6 weeks	35%	52.4	17	Good	1.4
23	0.4	7.1	1.9	3.8	48 hours	RT	6 weeks	51%	28.6	29	Good	2.5
24	0.4	7.1	1.9	3.8	73 hours	RT	6 weeks	51%	32.2	450	Good	2.2

References

1. James R. Griffith and John D. Bultman, Ind. Eng. Chem. Prod. Res. Dev. 17, 8 (1978)
2. Donald L. Hunston, James R. Griffith, and Robert C. Bowers, Ind. Eng. Chem. Prod. Res. Dev. 17, 10 (1978).
3. Don Dagani, C & EN, p.30 (July 14, 1980).