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OPTIMIZATION OF THE CS2 MANUFACTURING METHOD
II. EFFECT OF BLENDING TECHNIQUE ON CS2 TYPE 28

by

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July 1971

DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
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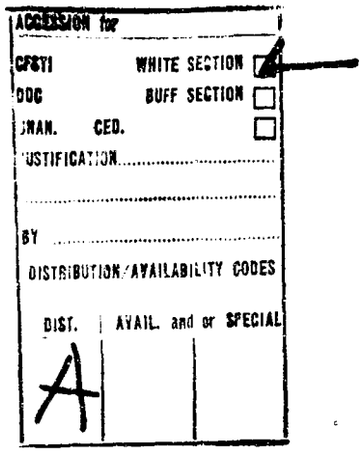

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13. ABSTRACT

The blending of hydrophobic silica additives with preground powders was studied. Drum type and twin shell blenders were used with and without additional energy sources to aid in deagglomeration and blending. Resorcinol and *o*-chlorobenzilidene malononitrile (CS) powders were used. The resultant powder blends were characterized by a variety of techniques. Properties studied included particle size, density, flowability, aerosolizability, reaerosolizability, and spreading rate on water. In addition, the resorcinol samples were examined in an electron microscope. A new procedure was used to permit examination of volatile solids in the electron microscope. The results of these experiments revealed that blending with additional energy to aid in deagglomeration produced a powder with superior properties. The electronmicrographs revealed that all the powder was coated with the silica, but that coated agglomerates were present in the blends. The additional deagglomeration energy reduced the quantity of agglomerates, thereby yielding more usable powder.

14. KEYWORDS

Blending	Density
CS2	Flowability
Powders	Particle size
Reaerosolizability	Electronmicroscopy
Resorcinol	Treated Cab-O-Sil

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FOREWORD

The work described in this report was conducted under Project 1B062116A081, Chemical Dissemination/Dispersion Technology (U). This work was started in February and completed in July 1969. The experimental data are recorded in notebooks 7840, 8027, and 8228.

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DIGEST

The blending of hydrophobic silica additives with preground powders was studied. Drum type and twin-shell blenders were used with and without additional energy sources to aid in deagglomeration and blending. Resorcinol and *o*-chlorobenzilidene malononitrile (CS) powders were used.

The resultant powder blends were characterized by a variety of techniques. Properties studied included particle size, density, flowability, aerosolizability, reaerosolizability, and spreading rate on water. In addition, the resorcinol samples were examined in the electron microscope. A new procedure was used to permit examination of volatile solids in the electron microscope.

The results of these experiments revealed that blending with additional energy to aid in deagglomeration produced a powder with superior properties. The electronmicrographs revealed that all the powder was coated with the silica, but that coated agglomerates were present in the blends. The additional deagglomeration energy reduced the quantity of agglomerates, thereby yielding more usable powder.

CONTENTS

OPTIMIZATION OF THE CS2 MANUFACTURING METHOD
II. EFFECT OF BLENDING TECHNIQUE ON CS2 TYPE 28

I. INTRODUCTION.

The blending of hexamethyldisilazane- (HMDS) treated Cab-O-Sil (colloidal silica from the Cabot Corporation, Boston, Massachusetts) with preground *o*-chlorobenzilidene malononitrile (CS) is a key step in the manufacture of agent CS2. In an earlier program,[1] some variations of CS2 blending techniques were given a cursory study. The results of the study were biased by a lack of knowledge of the problems relating to blending treated Cab-O-Sil into powders. This report covers a test program designed to optimize the manufacturing method used to prepare CS2 type materials.

In the first test series of this program, process type 26 (preblending unground CS with the treated Cab-O-Sil and then grinding the blend) was identified as the best technique.[2] However, process type 28 (grinding the CS first and then blending it with treated Cab-O-Sil) is the process most commonly used for large-scale manufacture of CS2. In this procedure the raw CS is ground in a jet mill to the desired particle size and then transferred to a blending apparatus. There it is mixed with the treated silica. Most of the blenders used are of the vertical mixing type in which the powders are tumbled by revolving the container around a horizontal axis. No outside energy source is used to aid blending or to deagglomerate the powder.

This experimental program was designed to investigate the effects of blending on the powders made by the type 28 process. Six blending procedures (described in table I) were used to prepare samples of CS and resorcinol (a CS simulant) powders treated with hydrophobic silica. The resulting powders were characterized using the tests developed for earlier studies[2] and a new reaerosolization test device.[3] In order to observe any variations in the coatings as a result of the blending process, electronphotomicrographs were made of the resorcinol powders.

II. EXPERIMENTATION.

A. Materials and Equipment.

Resorcinol (preground to 5 microns average size).

CS (preground to 5 microns average size).

Cab-O-Sil HS-5 treated with HMDS (Dow Corning Corporation, Midland, Michigan).

Burundum-fortified jar, size 00 (US Stoneware Company, Akron, Ohio).

Burundum-fortified rods, size 13/16 inch (Stoneware).

Solid rubber stoppers, size 5-1/2.

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[1] Wilcox, J. D., Klein, J. M., Hudson, F., Davis, P., Pistritto, J. V., and Harrison, J. EATR 4188. Preparative Techniques, Characterization Tests, and Results Used in the Selection of a Manufacturing Method for a Hydrophobic Treated CS(CS2). April 1968. UNCLASSIFIED Report.

[2] Klein, J. M., Nicolo, A., and Wilcox, J. D. EATM 141-3. Optimization of the CS2 Manufacturing Method. I. A Parametric Study. May 1969. UNCLASSIFIED Report.

[3] Hedley, W. H., Fearheller, W. R., Hansen, L. C., Long, R. L., Paullin, K. A., Richardson, G. A., and Sanders, D. L. Monsanto Research Corporation. Final Report. Contract DAAA15-68-C-0006. Studies of the Surface Chemistry of Solids in Dissemination. August 1967-February 1969. UNCLASSIFIED Report.

Table I. Blending Techniques

Sample No.	Type of blending	Extra mechanical help used	Powder charge	Blending time
				hr
		Barrel		
1	No. 00 ball Mill jar	None	95 gm Preground powder 5 gm HMDS-treated Cab-O-Sil	3.5
2	No. 00 ball Mill jar	7 Rubber stoppers No. 5½	95 gm Preground powder 5 gm HMDS-treated Cab-O-Sil	1.0
3	No. 00 ball Mill jar	7 Burundum-fortified porcelain rods, size 13/16	95 gm Preground powder 5 gm HMDS-treated Cab-O-Sil	1.0
		V-cone blender		
4	Plastic shell	None	190 gm Preground powder 10 gm HMDS-treated Cab-O-Sil	3.5
5	Steel shell	None	190 gm Preground powder 10 gm HMDS-treated Cab-O-Sil	3.5
6	Steel shell	High speed intensifier bar	1500 gm Preground powder 80 gm HMDS-treated Cab-O-Sil	0.1

Twin-shell blender ("V") (Patterson Kelly Corporation, Strousberg, Pennsylvania).

Dissemination evaluater (GCA Corporation, Bedford, Massachusetts).

Electron microscope (Norelco, Mount Vernon, New York).

B. Powder Sample Preparation.

Two basic blending methods were used in this study: drum blending and V blending.

In a drum type blender, the container is rotated around a horizontal axis, carrying the powder in a circular path. At some point along this path, gravity pulls the powder away from the drum, and the powder falls into the larger mass of material. Little blending takes place along the walls of the drum. This method of blending is relatively inefficient, and long blending times are needed to get a satisfactory product. The blending can be improved by the addition of a few grinding rods or other material, which will create localized stirring and shearing in the powder mass. The quantity of rods used is much less than that used in a grinding mill.

The twin-shell blender consists of two containers that are joined together in a V-shape (hence its common name) that rotates about an axis perpendicular to the plane that bisects the "V". This motion causes the powder in the blender to move in a three-dimensional pattern rather

than the circular pattern in the drum blender. In addition, the V-shape causes the sample to be split in half and then recombined with each 360° revolution of the blender. If desired, the rotation axis can be converted to a high shear zone by using a rapidly revolving bar that contains either pins perpendicular to the bar or blades set at an angle to the bar. In this way the blending can be accomplished very quickly and efficiently.

The powder samples were prepared from the same starting materials as shown in table I. The resorcinol and CS were preground to a particle size of approximately 5 microns using a fluid energy mill. The hydrophobic silica (HMDS-treated Cab-O-Sil) was prepared by Dow Corning.

C. Test Techniques.

Most of the methods and techniques used to evaluate these powder preparations have been described previously[2] and are listed in table II. A new reaerosolization test device, an improved version of the Monsanto Research Corporation reaerosolizer,[3] was used to measure this property of the powders.

From observations of the powders, it was apparent that there were numerous large lumps in some of the preparations. In order to determine the extent of these lumps, the powders were screened through No. 10 and 16 mesh screens. The amount of powder sample retained on each screen and that which passed through the screens was measured. To determine the composition of the sample retained on each screen, the quantity of resorcinol present was determined by ultraviolet spectrophotometry.

D. Electron Microscopic Examination.

Resorcinol and CS powders cannot be examined directly in an electron microscope because their vapor pressures at room temperature are too high. The material would volatilize completely in the vacuum chamber of the microscope. The procedure used to examine this type of material was developed specifically to minimize this problem.

Microscope grids were prepared using a carbon film supported on 200-mesh copper screen. The grids were examined in the electron microscope to insure the continuity of the carbon film. The resorcinol powders were aerosolized gently by tapping from a spatula and allowed to settle onto the grids. The grids then were placed on a stage in a vacuum chamber. The stage was cooled by passing liquid nitrogen through it, and then the chamber was evacuated. The grids were shadowed with chromium metal at an angle of 45° to 60°. The electronphotomicrographs of these shadowed grids were made in the usual manner. Only the resorcinol powders were examined using this technique.

III. RESULTS AND DISCUSSION.

The results of the powder characterization tests are presented in table II. In addition to the actual experimental results, a relative ranking was assigned to each test result with 6 being the best and 1 the poorest ranking. If two or more results were considered equal, the average ranking was given to each sample. In this manner, each experimental parameter was put on an equal basis. The sum of the performance rankings assigned to a powder showed the relative merits of the different preparative techniques. As can be seen from table II, the sample prepared in the V-blender using an intensifier bar was superior in performance. The samples prepared in the drum type mixers using rubber stoppers or rods were next in rank, and the plain samples were poorest.

The relative ranking system used to evaluate the powder properties has the advantage that it gives each test result an easily understood meaning. One need only examine the test results to see that high reaerosolizability and small particle size were considered to be desirable properties. This

Table II. Results and Performance Ranking

Characterization test	Powder preparation technique[a]					
	1	2	3	4	5	6
	Resorcinol blends					
Elutriation (GCA), %	25.41	24.46	25.05	21.28	22.93	24.04
Ranking[b]	5.5	3.5	5.5	1	2	3.5
Reaerosolizability						
@ 4850 cc/min, %	8.18	13.84	11.04	12.27	10.66	18.56
Ranking	1	5	3	4	2	6
@ 8050 cc/min, %	44.52	52.76	47.97	43.36	41.07	60.22
Ranking	2	5	4	2	2	6
Funnel flow, sec	12.2	7.4	7.0	48.6	34.8	6.2
Ranking	3	4.5	4.5	1	2	6
Fluid density, gm/cc	0.12	0.12	0.12	0.12	0.13	0.16
Ranking	2.5	2.5	2.5	2.5	5	6
Apparent density, gm/cc	0.27	0.25	0.25	0.24	0.25	0.41
Ranking	3	3	3	3	3	6
Bulk density, gm/cc	0.42	0.40	0.37	0.34	0.35	0.64
Ranking	4.5	4.5	2	2	2	6
Spreading rate, units X 10^{-6}	0.98	3.43	0.52	1.07	1.87	2.26
Ranking	2	6	1	3	4	5
Particle size						
mmd, microns	4.80	4.90	6.05	7.40	9.20	4.80
σ_g	1.79	1.86	1.92	2.12	2.01	2.00
Ranking	5	5	3	2	1	5
Sieving						
% on 10 mesh	12.1	0	0.0	8.0	5.9	–
% on 16 mesh	2.6	0.1	0.0	3.9	3.4	–
Ranking[c]	1	5	5	2	3	5
Ranking total	28.5	39	28.5	20.5	23	49.5
	CS blends					
Elutriation (GCA), %	50.73	62.88	52.12	58.99	58.24	64.54
Ranking	1	5	2	3.5	3.5	6
Reaerosolizability						
@ 4850 cc/min, %	14.26	11.25	11.04	9.23	10.88	7.39
Ranking	6	4	4	2	4	1
Funnel flow, sec	7.4	6.5	10.9	10.1	14.6	5.5
Ranking	4	5	2.5	2.5	1	6

[a]See table I.
[b]Highest ranking number is the best judged performance.
[c]Not used in total ranking as sample 6 was too large in size to sieve. Sample 6 contained no particles that would have been retained on either screen.

Table II. Continued

Characterization test/ranking	Powder preparation technique*					
	1	2	3	4	5	6
	CS blends					
Apparent density, gm/cc	0.20	0.22	0.20	0.18	0.19	0.35
Ranking	3	5	3	1	3	6
Bulk density, gm/cc	0.33	0.35	0.32	0.27	0.27	0.57
Ranking	3.5	5	3.5	1.5	1.5	6
Particle size, mmd, microns	7.4	10.4	8.4	9.1	10.9	6.3
Ranking	5	1.5	4	3	1.5	6
Ranking total	22.5	25.5	19.0	13.5	14.5	31.0

*See table I.

ranking also permits the experimenter to evaluate the significance of two similar experimental results. A minor disadvantage in the currently used ranking system is that all experiments are given equal weight. It may be possible in the future, after more experience has been gained with this type of powdered material, to assign relative weights to the different tests. For example, the funnel flow test might be given only half the weight of the reaerosolizability test. Until such time as enough experimental and field test data have been accumulated, equal weights will be assigned to each test parameter.

It is apparent from the results that preparative techniques using additional energy to deagglomerate the materials produced better powders. The V-blender equipped with a high-speed intensifier bar produces a zone of high shear in operation. As the powder passes through this zone, it is deagglomerated. In the drum blenders equipped with some grinding medium, the tumbling of the medium produces shear forces which deagglomerate the powder. (The amount of grinding medium used was much less than would be used for grinding purposes.) Better results were obtained using a soft medium (rubber stoppers) than with a hard medium (fortified porcelain rods). In addition to preparing a better powder, the use of outside energy to deagglomerate the powder also gives a larger quantity of usable powder product. As can be seen from the sieve experiments (first part of table (II), as much as 15% of the sample may be wasted as nonblended lumps or flips. The chemical analysis of the lumps and the resulting powder shows that the lumps are mostly pure substrate with, at most, only a coating of treated Cab-O-Sil, whereas the powder contains an excess of the Cab-O-Sil.

The electronmicrographs of the treated resorcinol powders (figures 1 and 2) are typical of the results obtained in this experiment. These photographs reveal that the powder sample is thoroughly coated with the silica particles. However, it can be seen that the coated particle may be an agglomerate. This observation explains some of the results that have been obtained. These agglomerates do not aerosolize as well as single particles. They do not spread on water as well as single particles. They are hydrophobic, however, and they do flow well in the funnel flow test. It is not possible to draw general conclusions from these results because the sample size is very small.

During the spreading rate experiments conducted with the resorcinol powders, it was observed that the powder skittered randomly over the water surface within the expanding circle. This observation may indicate that the powder surface is not completely covered, i.e., the powder is

Figure 1. Treated Resorcinol Blended in Plastic V-Blender

not properly blended. The skitte..ng may result from the localized dissolving of incompletely coated resorcinol particles. This subject is still under investigation.

There is no apparent difference between blending in a steel or plastic container. It is believed, however, that electrostatic buildup in the plastic container would be greater than in a steel container because of the different conductivities of two materials. It is suspected that the surface charge of the hydrophobic silica could have minimized any electrostatic effects.

The results of these two studies on optimization of the CS2 manufacturing process are as follows.

1. The type 26 process appears to give the best product.

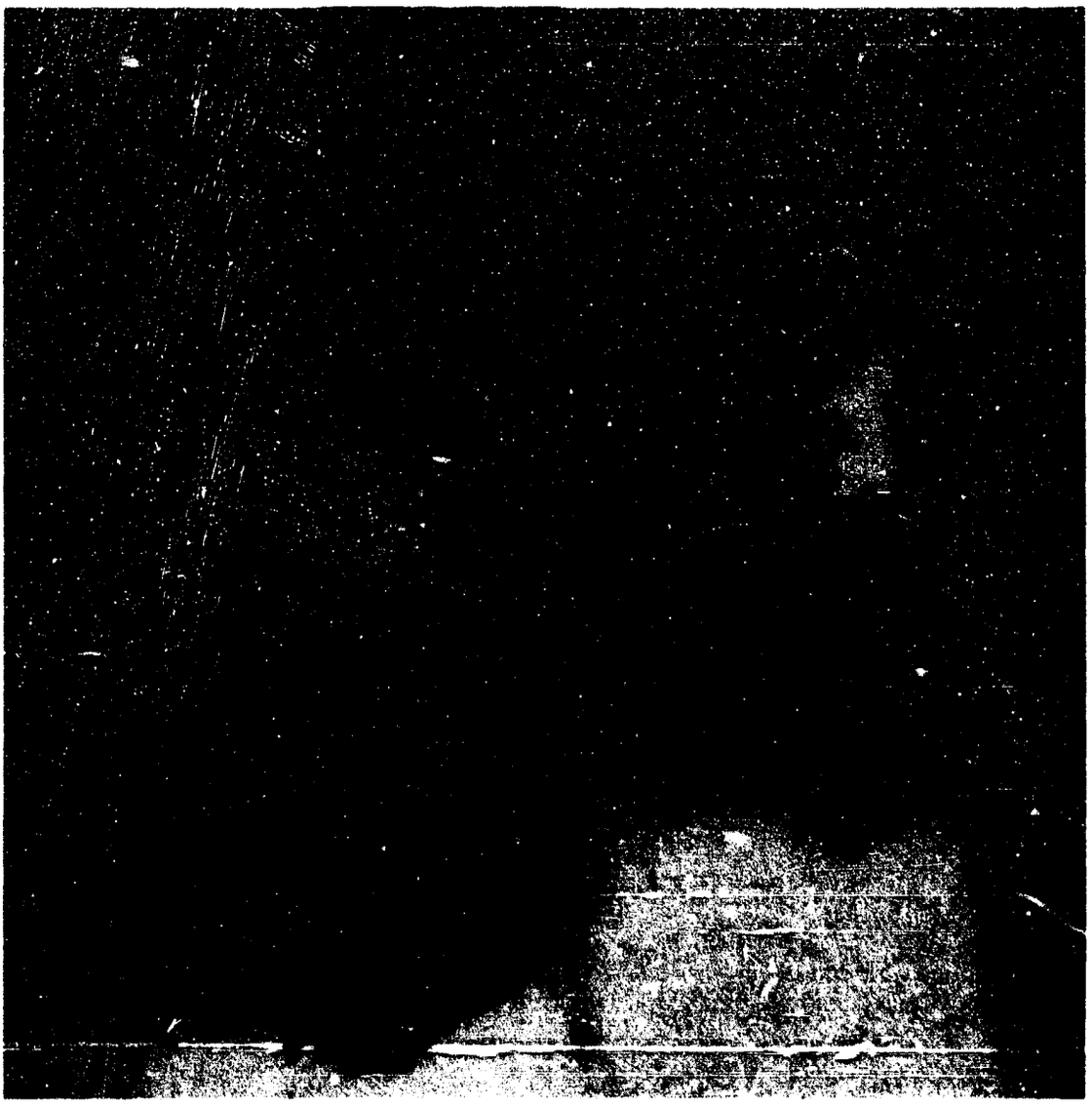

Figure 2. Treated Resorcinol Blended in Plain Drum Blender

2. When CS2 is made by the type 28 process, it is advisable to use some method of deagglomerating the powder (by applying the proper type of shear forces) that will result in a product superior to one made by a plain blending technique. If the deagglomeration is to be accomplished by the addition of a low density ball, pellet, or rod, the quantity of this mechanical blending aid should not occupy more than approximately 10% of the volume of the blender. This compares with 45% to 55% grinding medium (high density) used in grinding operations.

Regardless of what blending technique is used, a screen on the discharge part of the blender will not only retain the grinding media but will also retain undesirable chips or lumps of CS that have not been broken up during the blending operation.

It should be noted that the tests conducted represent the capability of the investigators in the field of powder technology. However, no one test has been developed that has a direct correlation with terrain denial. Efforts continue to develop such a test.

IV. CONCLUSIONS.

The preparation of CS2 by the type 28 process is enhanced if a proper source of deagglomeration energy is used during the blending process. A V-cone blender with a high-speed intensifier bar produced the best CS2 type material. Plain blenders, without a source of deagglomeration energy, produced inferior powders containing significant quantities of unblended material.