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**FORMULATION PROCEDURE AND
SPECTRAL DATA FOR A COATINGS
SYSTEM OPTIMALLY EMPLOYING
THE HIGH INTRINSIC REFLECTANCE
OF BARIUM SULPHATE**

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ABSTRACT

The use of polyvinyl alcohol as a binder for barium sulphate does not allow the intrinsically high reflectance of this material in the near vacuum ultraviolet to be optimally employed. In an effort to better utilize this property, completely inorganic coatings systems are described, where from the intrinsically high reflectance of barium sulphate in this spectral region can be gotten. Potassium sulphate turns out to be the preferred binder. Compositions, formulating procedures, and application techniques are included. For completeness, absolute and relative reflectance data are included for intra- and inter-system comparisons.

INTRODUCTION

In a previous paper of this series¹, the preparation and optical properties of a barium sulphate-polyvinyl alcohol coating were presented in detail. This system was formulated as a replacement for smoked magnesium oxide because it demonstrated improved stability toward atmospheric aging, significantly greater resistance to mechanical vibrations, while at the same time sacrificing a portion of the ultraviolet and infrared reflectances of smoked MgO. For most applications, it has turned out that this compromise is worthwhile. The weighting of the reflectance of a coating with respect to the extraterrestrial solar spectral irradiance is never dependent in a crucial way upon a highly reflecting coating below about 295nm, because less than four percent of the solar energy is summed below this wavelength. The situation for the infrared reflectance

is in some respects the reverse. Although 22 percent of the solar irradiance lies above 1200nm, requiring an accurate integration, the reflectance loss in the coating is compensated for by the relatively high intensity of infrared photon sources in this region, assuring that the detector responds linearly with regard to reflected energy over the wavelength range of 1200-2400nm.

Yet, for some unusual applications, the lowuv reflectance of barium sulphate-polyvinyl alcohol relative to smoked MgO is undesirable. Such an application involves the collection efficiency of a coating covering the internal surfaces of a chamber designed to detect Cerenkov radiation. To perform this function most efficiently, a coating, aside from reflecting electromagnetic energy dominantly in the diffuse mode, must possess the highest possible reflectance over that range of wavelengths of greatest interest for nuclear charge detection. This range happens to include energy from 200-500nm. To meet the requirement of high reflectance in the neighborhood of 200nm, it was judged that since the reflectance of high purity barium sulphate is comparable to smoked MgO, it should be used as the scatterer. Data given in the previous paper² shows that with polyvinyl alcohol as a binder barium sulphate does not approach its intrinsic reflectance in this region. From experience, it is already known that no binder organic in nature can give a coating whose reflectance at about 200nm compares favorably with the virgin powder.

In seeking out an optimum composition, two approaches come to mind. First, one can utilize the concept of differential solvent-solute vapor pressures

to deposit barium sulphate. This method is used successfully for sodium chloride; briefly, it involves the dispersion of sodium chloride in a system of liquids of differing vapor pressures with respect to room temperature so that 1) a minimal amount of salt is dissolved, 2) dry spraying is eliminated and 3) a considerable amount of ionic diffusion is permitted during evaporation of liquids to permit a partially amorphous salt structure to establish itself.

Secondly, one can utilize the concept of differential solubility. This concept mirrors the former in that a single solvent-dispersion medium is used wherein a material like the high purity barium sulphate with a polar surface is dispersed in, e. g., water along with a more soluble salt. In this case, 1) the solubility of one ingredient is required, 2) dry spray is minimal because the salts have negative free energies of hydration, and 3) the soluble salt crystallizes in the interstices between the barium sulphate particles giving a binding action, since self-crystallization is inhibited in the matrix. Both coatings do require primer systems because of their corrosive actions on commonly used metal substrates. The latter system is preferably applied over a specially chosen primer, since additional mechanical properties are acquired by the reflectance coating from the primer system.

In the next section, compositions are given for the coatings systems as well as methods of formulating and applying. Subsequently the chemistry of the paints are presented followed by a section giving optical data for comparisons with other systems.

COATING DEVELOPMENT

Prime Coat

Five mixtures of a prime coat consisting of high purity Al_2O_3 potassium silicate solution, $(0.35 [\text{K}_2\text{O} \cdot 3.3\text{SiO}_2]_{\text{MOLE}} + 0.65]_{\text{WT.}})$, and water were prepared by stirring with a magnetic stirrer in a beaker. After slurring was completed each was flow coated onto a glass slide, and allowed to dehydrate under ambient conditions or at 100°C . For the former samples one day was allowed for cure, while one hour was judged sufficient for the latter set. After each treatment, absolute reflectance measurements were taken. It was judged from these data that the ratio sequence of potassium silicate solution: Al_2O_3 : H_2O : : 1:3.3:7 was optimum.

Reflective Coating

Mixtures of $(\text{NH}_4)_2\text{SO}_4$, BaSO_4 , and water, as well as a saturated solution of K_2SO_4 and BaSO_4 were flow coated onto the optimum prime coat. Samples were cured similarly to the prime coat. Baking showed that as the coatings approached about 30-50 mils in thickness that samples became subject to bubbling and cracking. The optimum $(\text{NH}_4)_2\text{SO}_4$: BaSO_4 was determined to be 1:5 by reflectance measurements. However the BaSO_4 containing K_2SO_4 as the binder gave the greatest ultraviolet reflectance, and was therefore judged optimum overall.

PAINT PREPARATION

Prime Coat

To 35 parts of potassium silicate solution, $[0.35(\text{K}_2\text{O} \cdot 3.3\text{SiO}_2)_{\text{MOLE}} + 0.65\text{H}_2\text{O}]_{\text{WT}}$, 105 parts of Al_2O_3 , and 153 parts of water are added. The resulting mixture is then charged into a jar mill and milled for 1 hour. The milled slurry is then applied by spraying until a dry thickness of about 8 mils is obtained (about 16 wet), and allowed to air cure at least 24 hours before top coating. Air cure over a period of several hours is required to enable a good adhesive bond to develop between primer and substrate.

Reflective Coatings

A table listing compositions optimized according to physical and optical characteristics is given below. Systems with $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{SO}_4$ and K_2SO_4 , and K_2SO_4 are given for the sake of completeness. K_2SO_4 alone gives the highest ultraviolet reflectance.

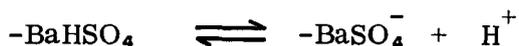
These compositions may be prepared by adding the soluble sulphate(s) to the required amount of water and stirring until a solution is obtained. Finally the BaSO_4 is added slowly and stirred until the composition is agglomerate free.

The coating is applied by spraying in one application if possible until a dry thickness of 8-30 mils is obtained depending upon application. For efficient ultraviolet scattering a nominal thickness of 8 mils is more than sufficient; however, for a reflectance maximum through to 2400nm thickness to 30 mils may be required.

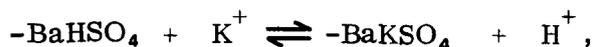
CHEMICAL ASPECTS

The preferable coating composition and the one likely to be most often utilized will be S2C, BaSO₄ plus K₂SO₄. However, because the composition has an acidic pH care must be exercised in its use, especially since the prime coat is porous. A saturated solution of K₂SO₄ has a pH of 5.8. A slurry containing BaSO₄ at a level of 72 parts in 108 parts of water reads normally 4.2. Combining the ingredients according to S2C give a resultant pH whose value decreases with time from 4.7 to a minimum of 3.5 over a period of weeks. If NaCl is substituted for K₂SO₄ on a mole basis, a pH of 2.3 results at stabilization. From tests of coatings containing NaCl over the alkaline primer applied to aluminum or iron, it became clear that an equilibrium pH of 2.3 is too low, because within a 24 hour time span the percolation of aluminum metal or iron hydroxide to the surface of the reflective coating became visually detectable.

Briefly, what is occurring in the reflective coating slurry is the exchange of protons and monovalent cations between BaSO₄ and solution. Schematically, say that



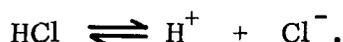
where -Ba represents a surface barium ion, then from the pH data it follows that when the solution contains K⁺ ions



that is, the equilibrium is shifted to the right side of the equation. The resulting pH for the coating composition is then dependent upon the ionization constant



or in the case of sodium chloride



For HSO_4^- , $K_a \cong 10^{-2}$ whereas for HCl , $K_a \cong 1$. This simple scheme explains the pH observation for the particular concentrations of ingredients chosen for the measurements. In general, measurements taken at such high concentrations are concentration dependent.

The primer on the other hand is an alkaline composition of $\text{pH} \cong 12$; for the composite system, therefore, we need to address ourselves to an acid-base system comprising a rather complex system of potassium salts not only of barium sulphate, but also of silicic acid and to a lesser extent aluminum oxide. Since the primer is water sensitive, application of the reflective coating with its lower pH causes the silicic acid and aluminum oxide potassium salts to discharge by releasing potassium ions in exchange for protons. By the common ion effect then, it follows that potassium sulphate will deionize and precipitate in the interstices of both coatings as well as in additional amounts onto BaSO_4 . Hence, the alkalinity of the prime coat serves to prevent the growth of potassium sulphate crystals, which, with the common ion effects derived from sulphate

as an intracoating effect and potassium as an intercoating effect, serves to gi
enhanced binding to the BaSO_4 powder.

RESULTS

Reflectance data for coatings discussed and briefly mentioned in previous sections are shown in graphical form in figures 1-4. Figure 1 shows reflectances for BaSO_4 coatings relative to BaSO_4 employing both potassium and ammonium sulphate as binders for two thicknesses. Data for the polyvinyl chloride (PVA) paint has been included for reference. Figure 2 is a plot of absolute reflectance for the systems given in figure 1 for a thickness of about 30 mils. Figure 3 compares five highly reflecting coatings now in use: barium sulphate-polyvinyl alcohol, MS-125, and the forerunner system developed by Eastman Kodak, smoked MgO, sodium chloride, and the potassium sulphate system described here over the alkaline primer. Figure 4, included for reference, compares to BaSO_4 polyvinyl alcohol powder, PVA paint (MS 125), high silica micro balloons, and millipore filter paper type EA.

COMMENTS

In offering a highly reflecting paint employing barium sulphate as the scatterer, and utilizing an inorganic binder rather than an organic one, e.g., polyvinyl alcohol, not only has the reflectance been improved down to about 200nm, but also the aging characteristics as measured by reflectance changes in the ultra-violet. From figure 4, PVA is seen to have significant uv absorption compared to barium sulphate, whereas potassium sulphate (not shown) should (intuitively)

have significantly less absorption. PVA can also react slowly with barium sulphate by esterification or transesterification reactions; such is not the case with potassium sulphate. Aging has not been observed in the inorganic system. On the other hand, the inorganic coating is more acidic than the mixed system, indicating that discoloration by corrosion could be a problem; the alkaline primer solves the problem nicely.

As with all highly reflecting coatings, care must be continually exercised to keep them free from atmospheric contaminants. As the uv reflectance is increased further and extended into the near vacuum ultraviolet, contamination will become more of a problem, since virtually all substances will degrade the performance of such a coating. Combinations of ingredients admixed from judicious choices according to the periodic table will not improve reflectance, since the combinations are limited. Films with improved reflectivity over comparatively narrow bands of wavelengths may likely have to be employed if further improvements are sought.

ACKNOWLEDGMENT

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Table I
 Compositions of BaSO₄ Coatings Using Sulphates
 With Monovalent Cations as Binders

Coating	(NH ₄) ₂ SO ₄	BaSO ₄	K ₂ SO ₄	H ₂ O
S2A	12.005	72.0	—	108.2
S2B	11.993	72.0	0.00851	108.0
S2C	—	72.0	1.014	108.0

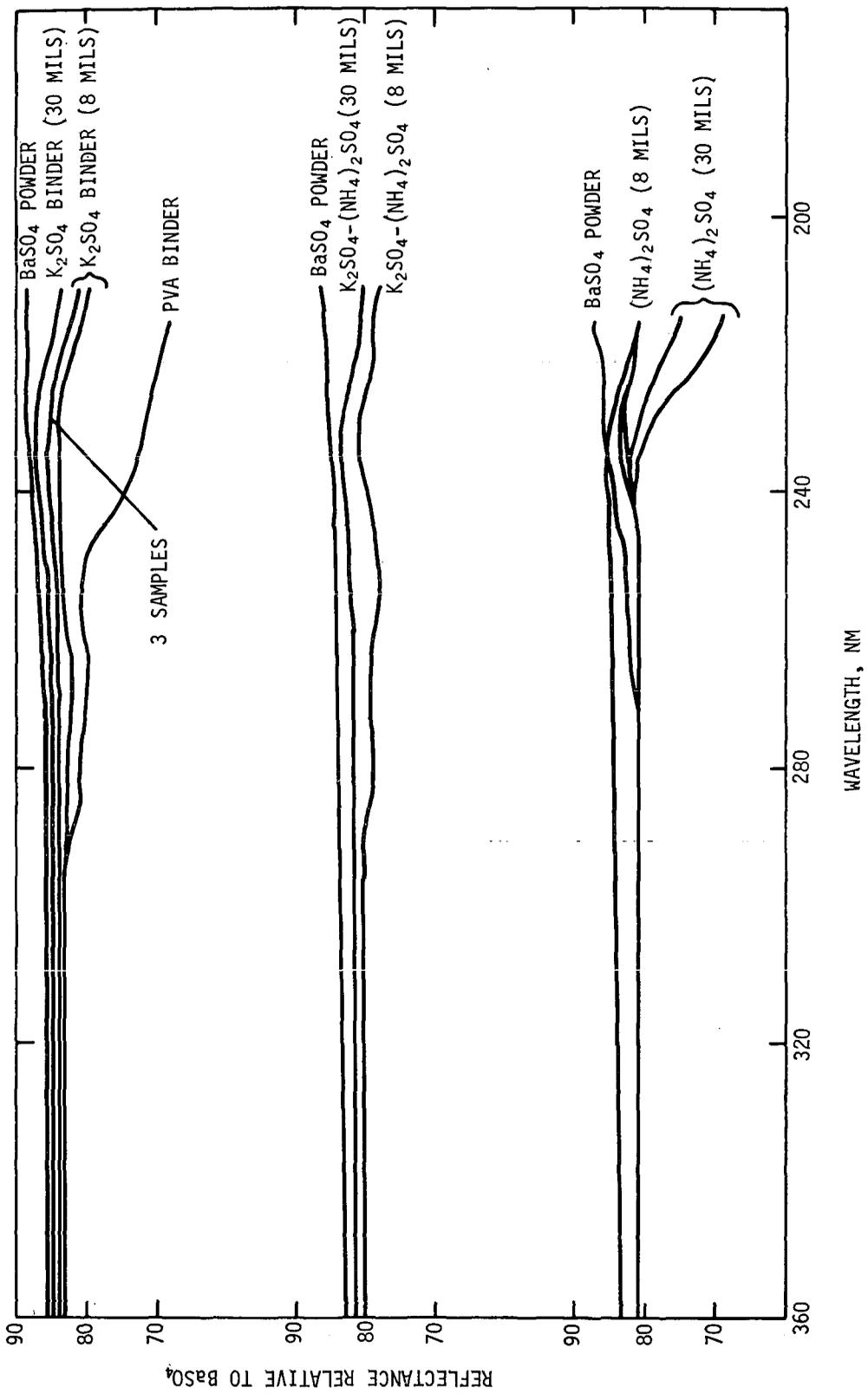


Figure 1. UV Reflectances of Barium Sulphate Coatings Employing Potassium Sulphate and/or Ammonium Sulphate as Binders

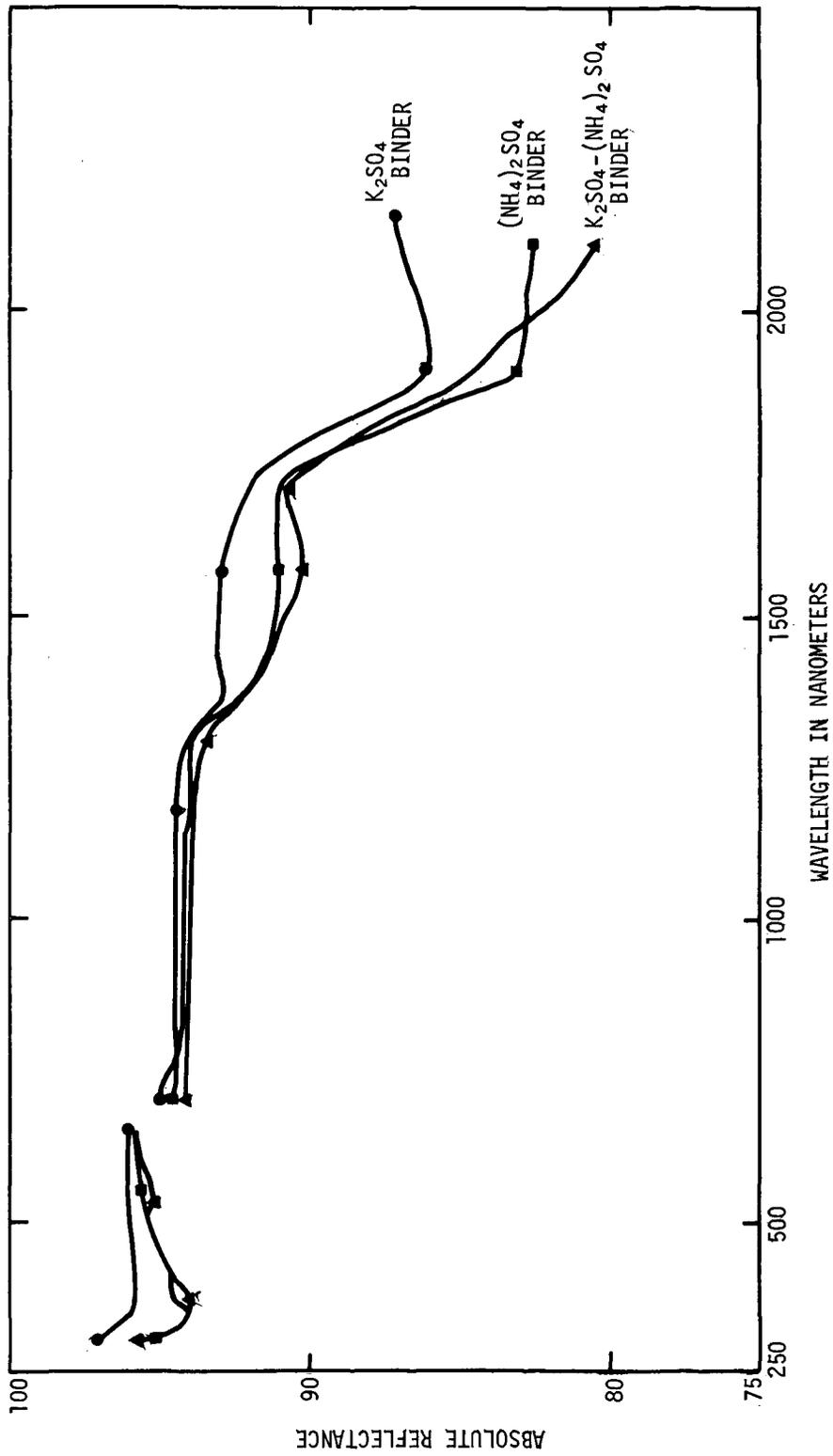


Figure 2. Comparison of Absolute Reflectances of BaSO₄ Coatings Employing Combinations of Sulphate Binders

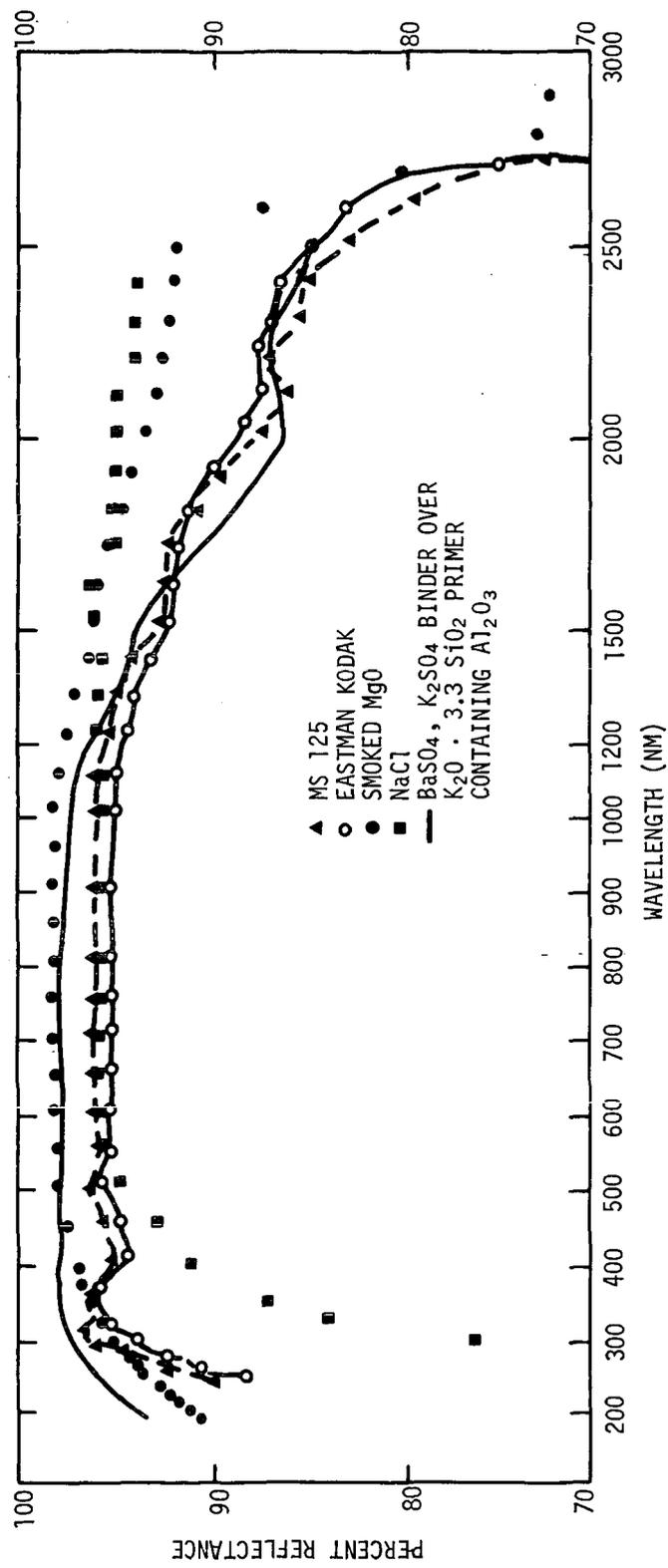


Figure 3. Comparisons of Spectral Reflectance Data for MgO, MS-125, Eastman White Reflectance Standard NaCl, and BaSO₄ - K₂SO₄

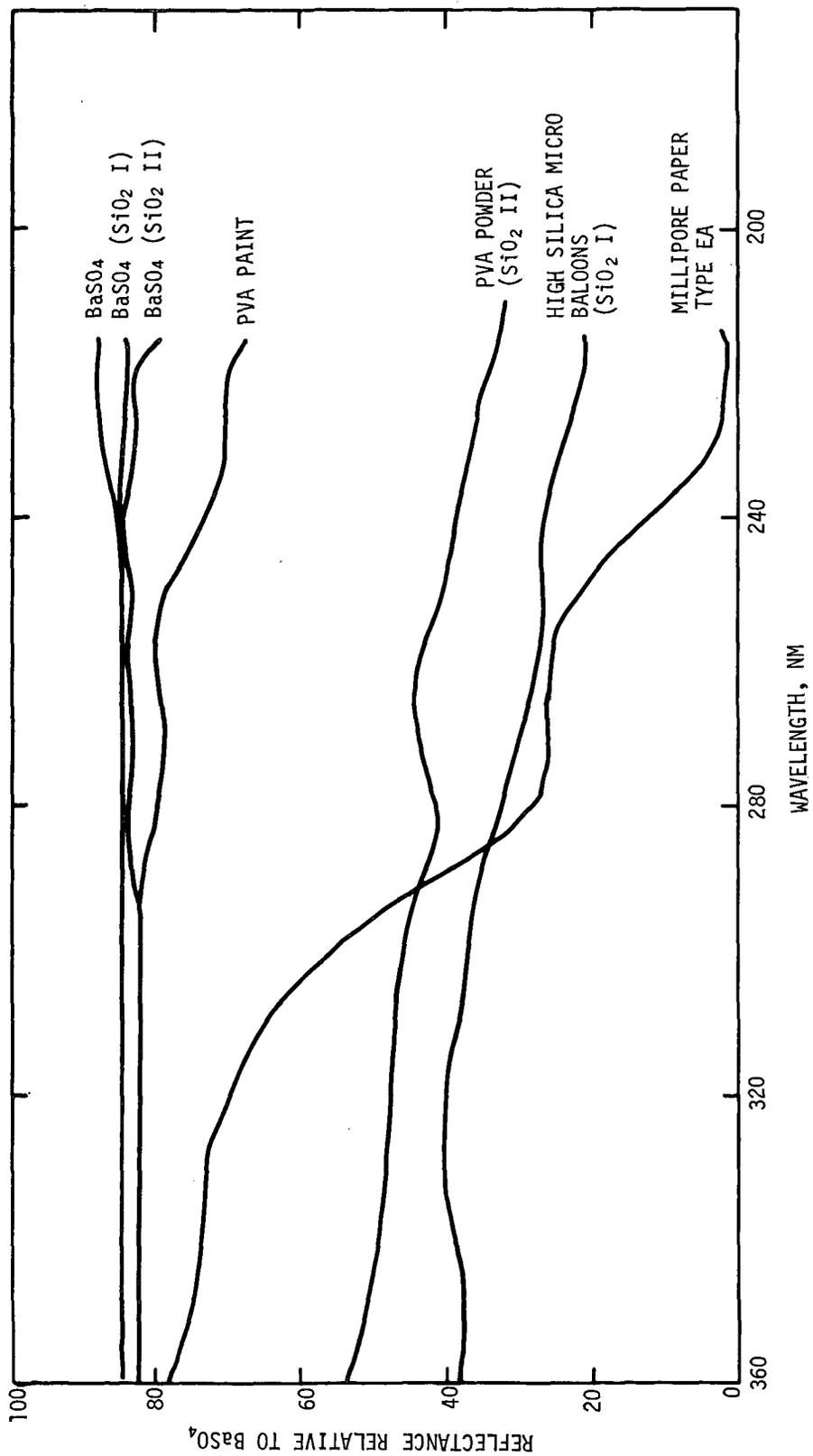


Figure 4. Curves Showing Relative uv Reflectance of Some Candidate Cerenkov Materials

1. Shal, C. M., and Schutt, J. B., "Formulation Procedure and Spectral Data for a Highly Reflecting Coating from 200 nm to 2300 nm." X-762-71-266
2. Ibid. p.6.