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EXPERIMENTAL STATION
RESEARCH AND DEVELOPMENT DIVISION TECHNICAL REPORT
CHEMICALS, DYES AND PIGMENTS DEPARTMENT
E. I. DU PONT DE NEMOURS & COMPANY

TiO_2 MICRONIZING AIDS

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Personnel:	J. B. Dunson, Jr., G. A. Schurr, J. O. Hitch, T. B. Ewell	

ABSTRACT

It has been shown that a micronizing aid reduces grinding energy by retaining chemisorbed water and/or hydroxyl on the pigment surface. This water and/or hydroxyl dissipates electrostatic charge developed during the shearing of the pigment and minimizes re-agglomeration. The effectiveness of micronizing aids has been empirically correlated to their known physical properties, and alternatives to the currently used aid, triethanolamine (TEA), are suggested.

N40794

I. INTRODUCTION

Triethanolamine (TEA) is used as a grinding aid to reduce micronizer steam on all plastic grade pigments but is used on only 6% of R-900, R-902 and R-960 production, due to its alleged incompatibility in certain customer formulations. A broadly applicable micronizing aid would not only reduce steam costs but could also reduce inventory costs by eliminating TEA-treated pigment package codes.

Lower micronizer steam/pigment ratios are needed to obtain equivalent gloss and dispersion when TEA is added to the pigment (1). Improvements in product performance due to TEA addition are:

- Higher gloss in solvent-based paints (1).
- Better dispersion in plastics (2) (3), solvents and waterborne paints(1).
- Prevention of yellowing in polyolefin plastics (2).

A survey of current literature, compiled by Dave Schussler, Chestnut Run, has shown many secondary references to TEA-related problems, but with very scanty documentation. He has confirmed, however, higher millbase viscosity in solution vinyls (4)(5), slight overbake discoloration for TEA codes in polyesters, and varying effects on the cure rates of acid catalyzed polyesters (6).

A large number of organic grinding aids have been tested in our department since ~1965. Reports on the most promising candidates are listed in the references (7-16). These include amines, polyols, polysiloxanes and azelates. TEA belongs to both the amine and polyol groups.

II. OBJECTIVES

These studies were initiated to develop a compatible TiO_2 treatment which will lower the amounts of steam required to micronize R-900, R-902 and R-960 pigments.

The approach was to define the mechanism by which TEA improves pigment gloss and dispersion in order to effectively choose new candidates and then select more compatible, non-amine aids, that would be expected to perform in a similar manner.

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III. SUMMARY & CONCLUSIONS

Evidence has been accumulated which shows that the role of the micronizing aid is to retain chemisorbed water and/or hydroxyl groups on the pigment surface. This water and/or hydroxyl dissipates electrostatic charge developed during the shearing of the pigment and minimizes re-agglomeration.

The effectiveness of a given micronizing aid has been found to be related to its boiling point, molecular weight and its number of functional groups. The functional groups are those which can interact with pigment chemisorbed water or surface hydroxyls and as such can be alcohols, amines, acids or esters. These parameters have been incorporated into an efficiency factor, viz. the micronizing aid efficiency factor (M.A.F.) and related to 30J gloss.

The effectiveness of different micronizing aids has been rated and compared to TEA.

Sorbitol is one of a series of predicted compounds which might replace TEA and be used to lower the S/P requirements of current production.

IV. PATENT SITUATION

1. Filing Action - No patent action is to be initiated at this time.

2. Patent Protection - We have no patents in force specific to use of TEA as a micronizer aid.

V. PROGRAM

The program is to determine micronizer steam reduction with potential alternative aids and to evaluate compatibility with a customer formulation where TEA is believed to cause problems.

VI. PUBLICATION STATUS

There are no plans to publish any portions of this work.

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VII. SPECIAL SAFETY PRECAUTIONS

The products formed are not toxic. The chemicals used to treat the pigment are handled in accordance with normal practices. However, in situations wherein the pigment gets airborne, dust masks and hoods are used. Gloves are worn for all chemical handling.

VIII. ENVIRONMENTAL CONSIDERATIONS

There are no pollution problems associated with this work that would not be considered normal in our pigment processing systems, in the laboratory or plant.

IX. ACKNOWLEDGEMENT

The writer gratefully acknowledges the assistance of J. B. Dunson, Jr., and G. A. Schurr of the Engineering Department for the experimental work on the ETC micronizer. He is also thankful to C. V. Miller and J. O. Hitch for analytical assistance, and to T. B. Ewell for his diligence in this work.

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DISCUSSION

TiO_2 particles have regions relatively rich in Al_2O_3 within a matrix relatively poor in Al_2O_3. These aluminum-rich "islands" will be p-type semiconductors with different values of work function, resistivity, and dielectric constant than the n-type semiconductor matrix. As a result, there should be a polarization of charge within the particle which will generate non-uniform external electric fields. The edges of the "islands" will be strongly reactive chemically due to local electron density gradients. Particles as a result can be held together not only by short range Van der Waal's forces, but also by Coulombic forces capable of relatively long range interactions between "island" edges on adjacent particles.

Not only should more work be required to micronize polarized particles than nonpolarized particles (due to differences in work function and dielectric constant), but due to the high resistivity of the TiO_2 matrix the sheared particles will tend to have equal and opposite charges and try to reagglomerate. If the particles are separated more rapidly than electrons (or holes) can move to cancel the polarization, the separated particles will bear equal and opposite charges. The pertinent electrical time constant is called the "charge relaxation time constant" and is numerically equal to the product of the permittivity of the material with its resistivity.

The role of TEA then could be to reduce the TiO_2 surface resistivity and its charge relaxation time constant. Amine nitrogen (Lewis base) could react with "island" edges (Lewis acid). The resulting shift in TEA electron density would permit the ethanolic hydroxyls to function as weak Lewis acids and bond locally with the TiO_2 matrix (n-type semi-conductor = weak Lewis base). The resulting relatively conductive organic network would permit charge to migrate much more rapidly even with only a fraction of a mono layer coverage. This could be a bulk or localized phenomenon.

A. Conductivity Measurements

Electrical conductivity measurements showed that TEA treated TiO_2 did not permit the more rapid dissipation of charge than non-treated samples. TEA treatment lowered the bulk conductivity of a TiO_2 particle (Fig. I). The charge relaxation time constants (i.e., the time it takes for an electrostatic charge to migrate across a unit surface) are from 1 to 100 seconds for TEA treated samples; and from 1 to 10 seconds for control R-900. (The time it takes to shear an agglomerate is estimated to be of the order of 0.1 to 1 millisecond).

These results do not preclude, however, that TEA may still be influencing the build-up and dissipation of charge in localized areas of the pigment.

Experiments were set up at the Engineering Test Center micronizer to answer this question.

B. Engineering Test Center Micronizer Tests

The purpose of this investigation was to determine:

1. if electrostatic charge can be detected and measured during the micronization of pigment.
2. if this charge was related to the efficiency of pigment micronization.
3. if the charge can be controlled by an external electric field.
4. the factors which influenced the charge.
5. the effects of TEA.
6. if micronizer parameters can be adjusted to give R-900 dried discharge (D.D.) micronizer efficiencies equivalent to TEA treated R-900 DD.

The Engineering Test Center (ETC) micronizer is a single stage, single pass unit with a 0.161 inch sonic nozzle (Fig. II). It is equipped with two spark plugs at the throat of the nozzle. They are connected to a 6000 volt transformer capable of generating 0.40 milliamps current. An electron probe (connected to an electrometer) is located at the entrance of a 3 to 5 micron rated cyclone. The probe can detect and measure net electrostatic charge. Micronizer efficiency is determined by the amount of sample passing through the cyclone and collected in the second stage Dacron® Twill bag filter. Typical 30J gloss values for R-900 collected in the second stage filter are 74 to 76 and for the pigment collected in the cyclone, 24 to 26.

The results of this investigation from over fifty treated and non-treated pigment samples micronized showed:

1. Electrostatic charge was detected and measured during the micronizing of R-900 DD and TEA treated R-900 DD.

2. This charge was related to the efficiency of the micronizer. The smaller the net charge measured on the pigment, the greater was its efficiency (Fig. III). This effect was essentially independent of the presence of TEA, the steam to pigment ratio, the temperature of the stream or the thermal history of the TiO_2.

3. The micronizer efficiency could not be significantly altered through the application of external electric fields. The calculated repulsive forces between particles as a result of these fields should have been in excess of the attractive forces between the particles (Appendix I).

4. The electrostatic charge was significantly influenced by:

   a. the water content of the pigment, i.e., temperature of the pigment before micronization - the higher the temperature, the higher the net charge and the lower the efficiency of the micronization (Fig. IV).

   b. the relative humidity of the steam (steam temperature) during micronization - the lower the temperature, the smaller the net charge and the higher the efficiency (Fig. V).

   c. the S/P ratio - higher charge and lower efficiency were observed for feed ratios above and below 200 g/minute, (S/P = 1.7).

   d. the presence of TEA which decreased the net electrostatic charge and increased efficiency, Table I.

Table I shows that at S/P ratios $\leq$1.7, R-900 DD can be as efficiently micronized as TEA treated R-900 DD under conditions which maximize the water content of the pigment - no preheat treatment and low steam temperatures $\leq$350°F. Under conditions which facilitate dehydration of the pigment - preheat treatment or steam temperature $\geq$350°F - the performance of either pigment can be degraded, R-900 DD more so than TEA treated R-900 DD.

At S/P ratio >1.7, TEA treated R-900 is micronized more efficiently than R-900 DD. The efficiency at which R-900 DD could be micronized could not be increased to that of TEA treated R-900

by pretreating the R-900 DD, e.g. 90°C, 20% relative humidity. Under conditions which facilitate dehydration of the pigments, the performance of both pigments were degraded, R-900 DD more rapidly than TEA treated R-900 DD.

C. Edge Moor 8-inch Micronizer Tests

Results on the Edge Moor 8 inch micronizer confirm the above effect of pigment moisture on 30J gloss, Table II. The effect was smaller for the TEA pigment than for the non-treated pigment. No trends dependent upon steam temperature (relative humidity) could be detected at any pigment moisture level on this equipment. Efforts to improve the gloss of R-900 DD by varying the moisture content of the pigment, e.g., pre-treatment at 90°C, 20% R.H., failed to match the efficiency of the TEA treatment.

D. Thermogravimetric Analysis (desorption)

Thermogravimetric data were obtained on a series of pigments treated with micronizing aids reported in the literature. The data show that micronizer aids minimize the TGA weight loss (presumably water) of a pigment. The weight loss has been related to the 30J gloss of the pigment. The relationship is independent of the micronizer aid employed. The smaller the weight loss at a given temperature, e.g. 200°C, the higher the 30J gloss of the pigment, Fig. VII. Typical TGA curves are illustrated in Fig. VIII for ethanolamine, diethanolamine and triethanolamine.

This result supports the hypothesis that TEA functions by retaining water in the pigment surface which in turn helps to dissipate electrostatic charge.

E. Thermogravimetric Analysis (adsorption)

Additional evidence was compiled which shows that the amount of TEA adsorbed by the pigment and the effectiveness of TEA as a micronizing aid are proportional to the amount of surface hydroxyl or chemisorbed water on the pigment.

The TEA adsorbed by R-900 coated with boehmite, trihydrate or an amorphous alumina at 150°C has been measured, Table III. Similar measurements were made on R-960. The boehmite R-900 had a higher affinity for TEA than the corresponding trihydrate or

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amorphous alumina at this temperature. The boehmite alumina R-900 also requires higher temperatures than the trihydrate or amorphous alumina to remove its chemisorbed water, Figure IX. Thus the amount of TEA adsorbed is in proportion to the residual chemisorbed water on the sample. The TEA adsorption by the boehmite alumina coated R-900 was also measured at 100, 150, 200 and 250°C, Table III. The amount of TEA adsorbed decreased with increasing temperature. At temperatures above 250°C, little or no adsorption was observed. This, however, is probably not only due to the loss of surface hydroxyl but also the result of increasing TEA vapor pressure and lower sticking coefficient. Therefore, the TEA adsorption by boehmite coated R-900 was measured after the sample had been heated to 600°C in dry nitrogen. The dehydrated pigment had a significantly smaller amount of TEA adsorbed, Table III.

The above results are consistent with the effect observed on the Engineering Test Center and Edge Moor 8-inch micronizers where dehydration of the pigment before the addition of TEA minimized the effectiveness of the TEA treatment and degraded the 30J gloss of the pigment.

This is also shown in Figure X where the TGA weight loss of pigments treated with different amounts of TEA is recorded. The larger the amount of TEA, the smaller the weight loss and, referring to Fig. VII, the greater the 30J gloss.

The above hypothesis can be summarized as such: The amount of TEA adsorbed by the pigment is proportional to the residual surface hydroxyl on the pigment. The effectiveness of TEA as a micronizing aid is a result of it minimizing the loss of the surface hydroxyl during micronization.

It was also noted that TEA does not significantly adsorb onto R-960 pigment or pigment coated with amorphous alumina such as R-931. It utility as a micronizing aid for these pigments is therefore questionable. This has been reported by other investigators. In these experimental runs, the TEA was heated to 90°C and passed over the TiO_2 samples through dry nitrogen.

F. ALTERNATES TO TEA

Other high boiling, low molecular weight compounds which could adhere to the pigment chemisorbed water or hydroxyl functionality were evaluated.

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A brief review of the literature revealed that the mono- and di-carboxylic acid hydrocarbons met many of the requirements. The TGA adsorption at 150°C for these and other aids, Fig. VII, was determined for boehmite alumina coated R-900. Table IV shows the materials. Fig. XI shows that the amounts adsorbed were directly related to the boiling point of the material independent of alcoholic, amine or carboxylic acid functionality. There was no adsorption of a high boiling compound with only hydrocarbon functionality, viz. nona-decane (B.P. 330°C).

It appeared, therefore, that the effectiveness of a micronizing aid should be related to its boiling point, inversely related to its molecular weight, and directly related to its number of functional groups. High boiling point compounds are required in order to permit condensation - sticking - of the compounds to the surface water or hydroxyl group. Low molecular weight compounds are required to maximize the number of moles of the aid and multi-functionality to interact with the maximum number of hydroxyl groups. The functionality could therefore be an amine, ester, acid or polyol, etc.

Table V is the result of an effort to rate the efficiencies of micronizing aids evaluated based on the above criteria. The efficiency of each aid is estimated as its boiling point or decomposition temperature divided by molecular weight times the number of functional group and is represented as M.A.F., Micronizer Aid Efficiency Factor. The only micronizer aid illustrated with an M.A.F. greater than TEA (M.A.F. = 7.21) is pentaerythritol (M.A.F. = 8.40). After TEA is trimethylol propane (M.A.F. = 6.2). The next six micronizing aids has M.A.F.'s closely grouped between 4.0 and 5.0. The remaining aids have M.A.F.'s below 3.50. From this table only pentaerythritol and trimethylol propane should be suitable replacements for TEA. There are, however, problems in coating pigment with pentaerythritol because of its high melting point, 262°C, and limited solubility in common solvents.

Fig. XII is a plot of 30J gloss versus the M.A.F. for many of the micronizing aids evaluated. The pooled standard deviation of the 30J gloss measurement is 2.3. The 30J standard deviation for this correlation is 2.8. The correlation coefficient is 0.92.

These results indicate that the best micronizing aids would be those with the largest number of functional groups and the lowest total molecular weight for a given boiling point. Ideally this corresponds to a compound composed solely of functional groups. The functional group number - molecular weight ratio could then be expressed as n over n times "F" where n is the number of functional groups and "F" is the formula weight of each group. This ratio would be a constant for each functional group. The M.A.F. could then be expressed as the boiling point times the constant.

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Table VI lists the reciprocal formula weights of the basic units containing the functional groups which make up the molecular weight of a micronizing aid. Also listed are the boiling point ranges required by compounds to have an M.A.F. greater than TEA - assuming that all the functional groups indicated can interact with pigment surface hydroxyl. Table PGS-I explains why alcohols and amines have been the preferred micronizing aids - their reciprocal formula weights are the highest. Also, the literature boiling points of compounds associated with the other functional groups are well below those required - with the exception of the silicones.

A review of the literature shows that some of the best non-nitrogen containing candidates for a new micronizing aid are the polyols: d-glucose, meso-erythritol, sorbitol and galactitol (Table VII). These compounds are water soluble and melt below the temperatures associated with micronization.

G. EVALUATION OF ALTERNATIVES

The 30J gloss of R-900 pigment treated with the above aids and their costs are shown in Table VIII. All 30J glosses were equivalent to or better than the gloss of the TEA treated sample with the possible exception of d-glucose where some decomposition was noted. Overall, sorbitol is the lowest in cost of this series and would be the best alternative to TEA.

TGA data also confirms these findings. Previous tests showed that the weight-loss of a treated pigment at 200°C is inversely related to the 30J gloss of the pigment. The weight losses at 200°C for the experimental pigments were almost identical, Fig. XIII, and smaller than for the TEA treated pigment, Fig. XIV.

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APPENDIX

REPULSIVE AND ATTRACTICE FORCES BETWEEN PIGMENT PARTICLES

The estimated number of 1 micron TiO_2 particles at a feed rate to the micronizer of 200 grams per minute is 1.5×10^{12} particles per sec.

With a corona current from both spark plugs of 0.45 milliamperes, the electron flow per second is calculated to be 2.8×10^{15} electrons/sec.

The number of electrons generated per 1 micron particle is thus approximately 2×10^{3}.

The repulsive force between two particles, each with an electrical charge of 100 electrons, (100 is the maximum number possible on a 1/2 micron diameter particle without establishing corona) is 2×10^{3} dynes/cm^2.

$$F = \frac{q_1 \times q_2}{4\pi\varepsilon \times h^2}$$

F = force in Newtons
q = charge in coulombs
ε = absolute dielectric constant of media in farads/meter
h = separation between particles - meters (assume 1/2 μ)

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$$F = \frac{(100 \times 1.6 \times 10^{-19})^2}{4\pi \times 8.85 \times 10^{-12} \times (0.5 \times 10^{-5})^2}$$

$F = 9.3 \times 10^{-12}$ Newtons $\times 10^5$ dynes/Newton $= 9.3 \times 10^{-7}$ dynes

The area of 1/2μ particle $= \frac{\pi d^2}{4} = \frac{\pi}{4} \times (.25)^2\ \mu^2 \times 10^{-8}\ cm^2/\mu^2$

$= 4.68 \times 10^{-10}\ cm^2$ cross section area

Force per unit area $= \frac{9.3 \times 10^{-7}}{4.68 \times 10^{-10}}$ dynes $= 2 \times 10^3$ dynes/cm^2

The attractive forces between particles as Lifshity* calculates as 0.093 dynes/cm^2.

$$F = \frac{hc}{H^4} \frac{\pi^2}{240} \left(\frac{\varepsilon_o - 1}{\varepsilon_o + 1}\right)^2 \phi\ (\varepsilon_o)$$

h = Planck's const.-erg-sec.
c = Velocity of light-cm/sec
H = Particle separation dist.-cms
ε = Static dielectric const.
ϕ = Const. (value from Tables)

calculated for a particle 1/2μ apart

$$F = \frac{6.62 \times 10^{-27} \times 3.0 \times (3.14)^2}{(5)^4 \times 240} \left(\frac{79}{81}\right)^2 \times 0.77$$

$F = .093$ dynes/cm^2

Less than 5 electrons per particle would have been required to make the repulsive forces smaller than the attractive forces.

$$F_{(5\ \text{electrons})} = 2 \times 10^3 \times \frac{(5)^2}{(100)^2} = .049 \text{ dynes/cm}^2$$

*Soviet Physics, Vol. 2, No. 1, January 1956, "The Theory of Molecular Attractive Forces Between Solids".

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INDEXING TERMS

TEA

Micronizing Aid

Electrostatic Charge

Effect of Moisture

New Micronizing Aids

TiO_2

Grinding

R-900

Figure I

Resistivity vs. Reciprocal Degrees Kelvin

For R-900 Pigment

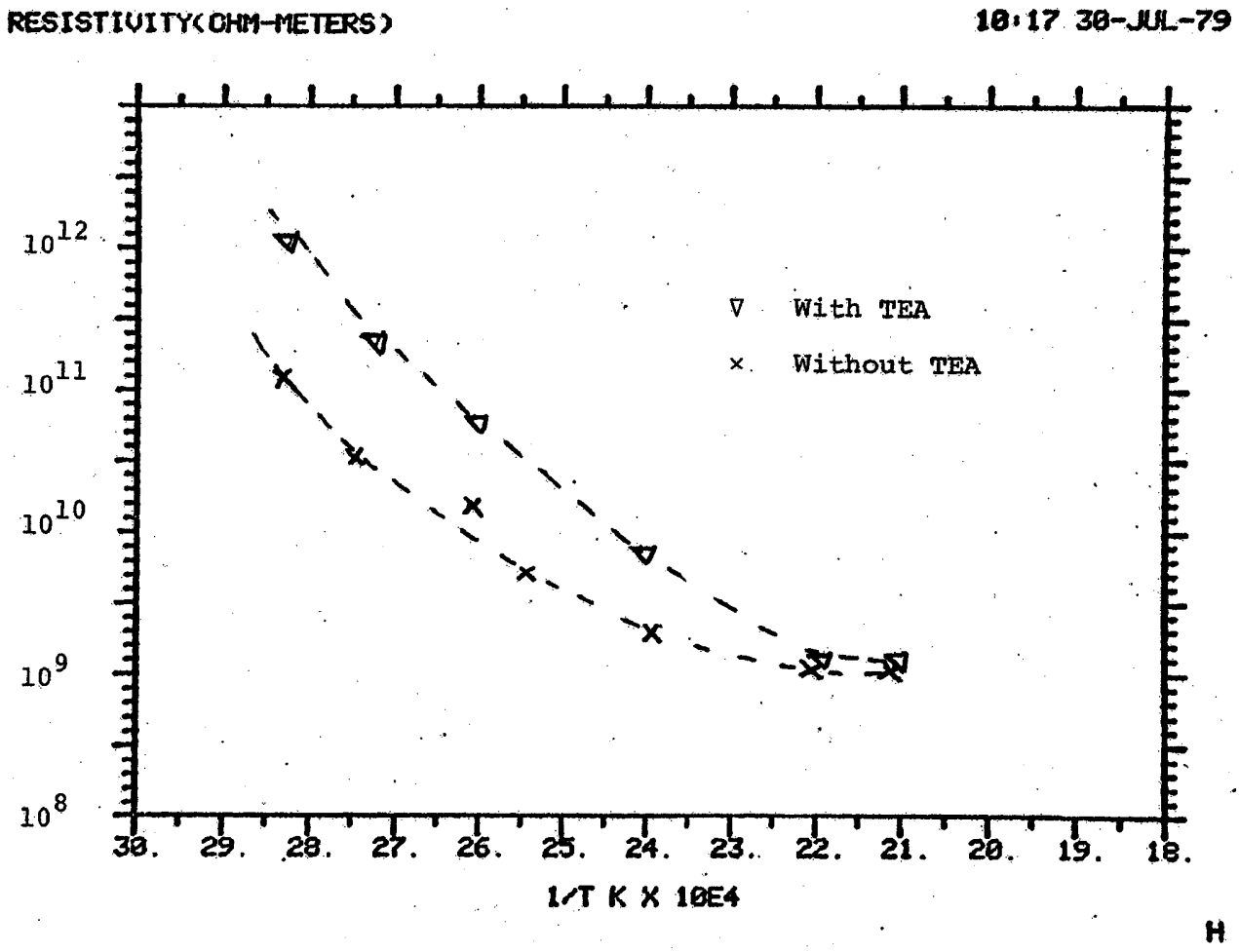
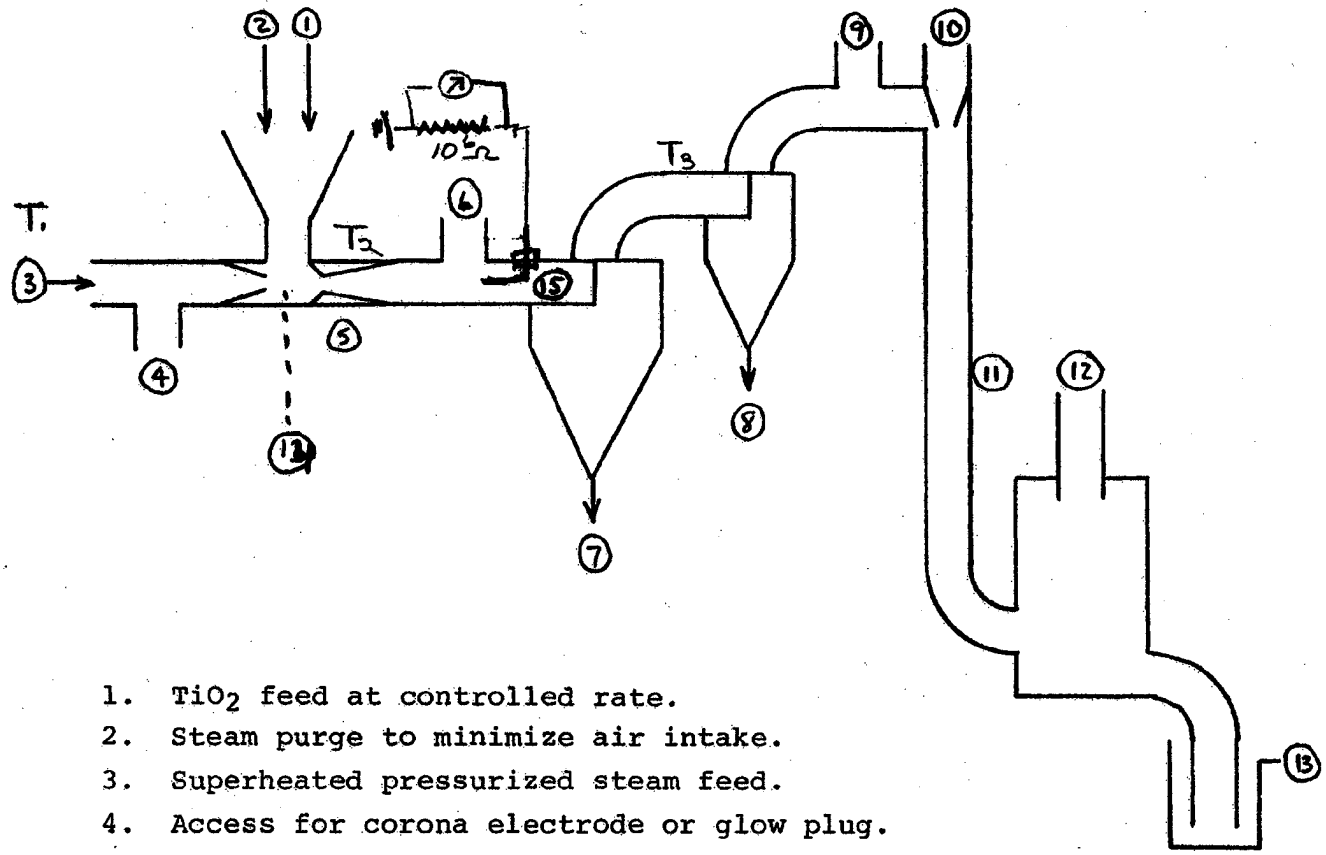


Figure II
Engineering Test Center Micronizer



1. TiO_2 feed at controlled rate.
2. Steam purge to minimize air intake.
3. Superheated pressurized steam feed.
4. Access for corona electrode or glow plug.
5. Alternative dielectric or conductive throats.
6. Access for charge or mass sampling.
7. Coarse fraction from primary cyclone.
8. Fine fraction from secondary cyclone.
9. Access for charge or mass sampling.
10. Scrub water feed.
11. Pipeline scrubber/condenser.
12. Air vent to vacuum system through meter.
13. Whitewater from hotwell.
14. 2 Champion spark plugs 0.050 gap 0.40 milliamps
15. 1/4" stainless steel probe in Teflon® jacket.

Electrically isolatable components (>10 meg ohms to ground when analyzer circuit is open)

- corona charger
- venturi throat
- cyclones
- steam nozzle
- charge analyzer
- charge analyzer

Figure III

ETC % Efficiency vs. Microamps in Shear Zone

For R-900 DD

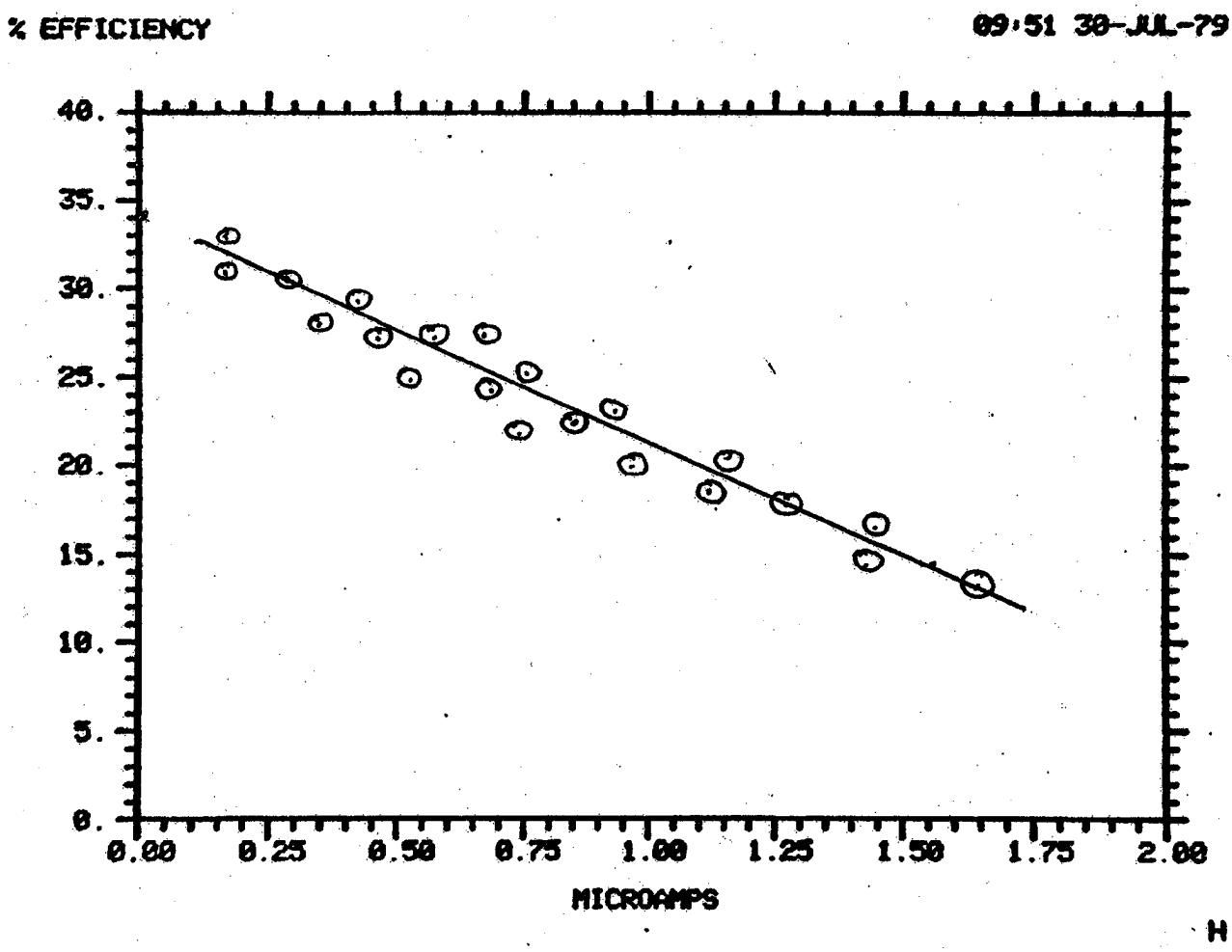


Figure IV

ETC: Microamps and % Efficiency
vs.
Pigment Preheat Temp. °F
For R-900 DD Pigment

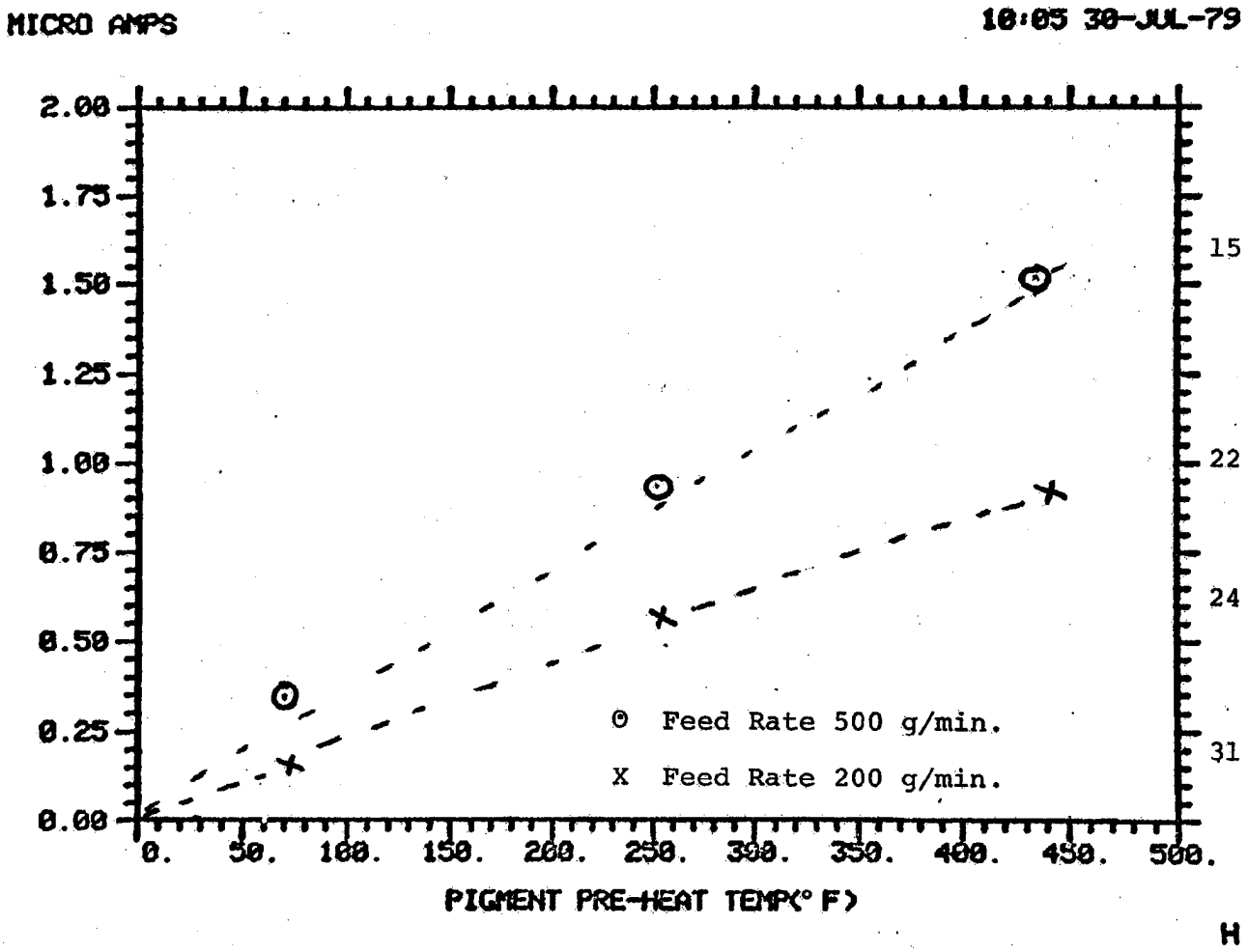


Figure V

ETC Microamps and % Efficiency
vs.
Steam Temp. °F_2
For R-900 DD Pigment

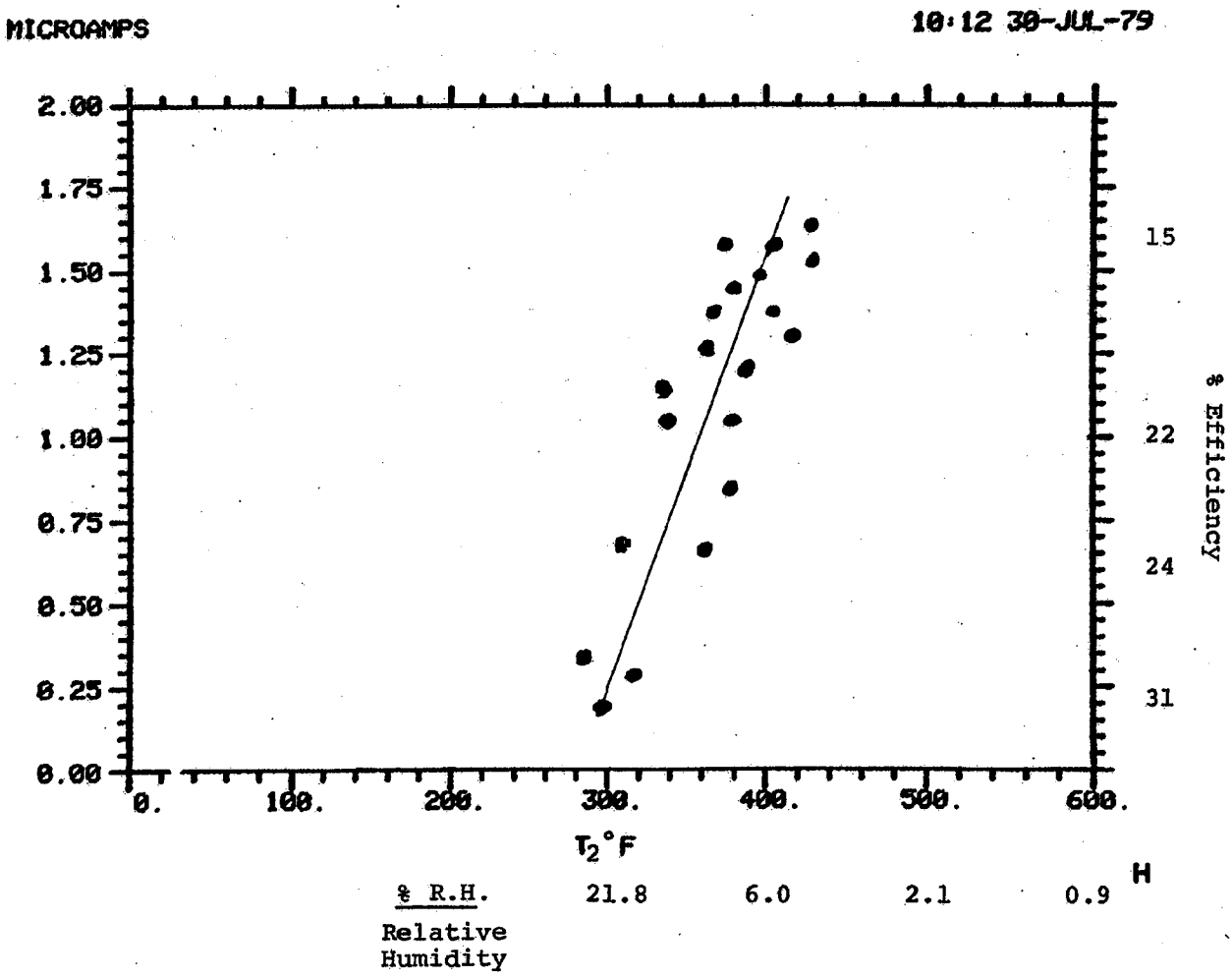


Figure VI

ETC Microamps and % Efficiency
vs.
Feed Rate

Steam to Pigment Ratio
For R-900 Pigment

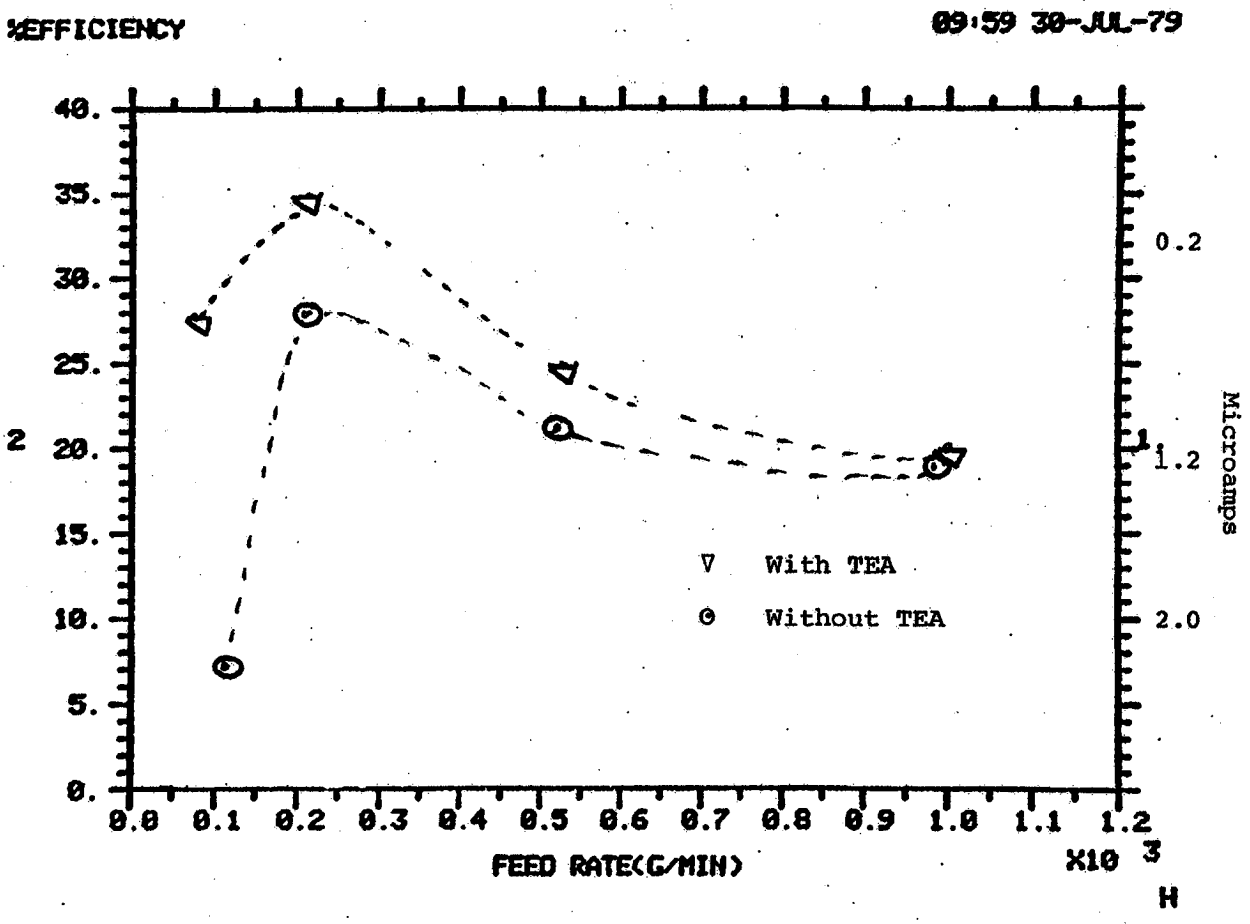


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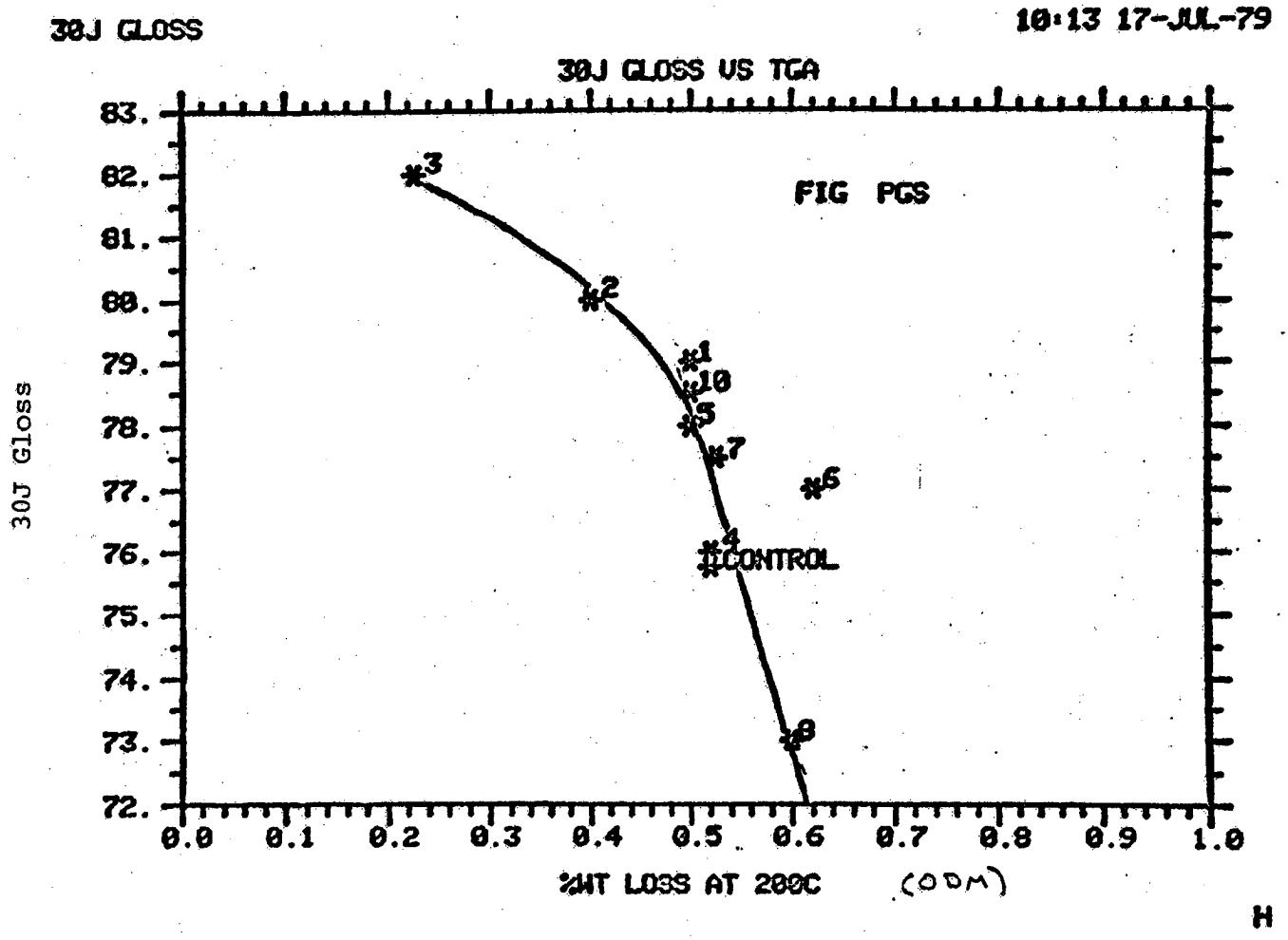
FIGURE VII

30J Gloss vs. TGA Weight Loss 200°C
For R-900 Pigment and
Micronizer Aids (0.5%)



MZR Aid (0.5% weight)

1) Ethanol Amine
2) Diethanol Amine
3) Triethanol Amine
4) Trimethanol propane
5) Pentacrythritol
6) AMP
7) Nitrilo triacetic acid
8) Dioctyl azelate
9) Control
10) TEA (.25% weight)

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Figure VIII

TGA Mass Loss vs. Temperature

MZR. Tri-Di-Mono-Ethanol Amines
on R-900 Pigment

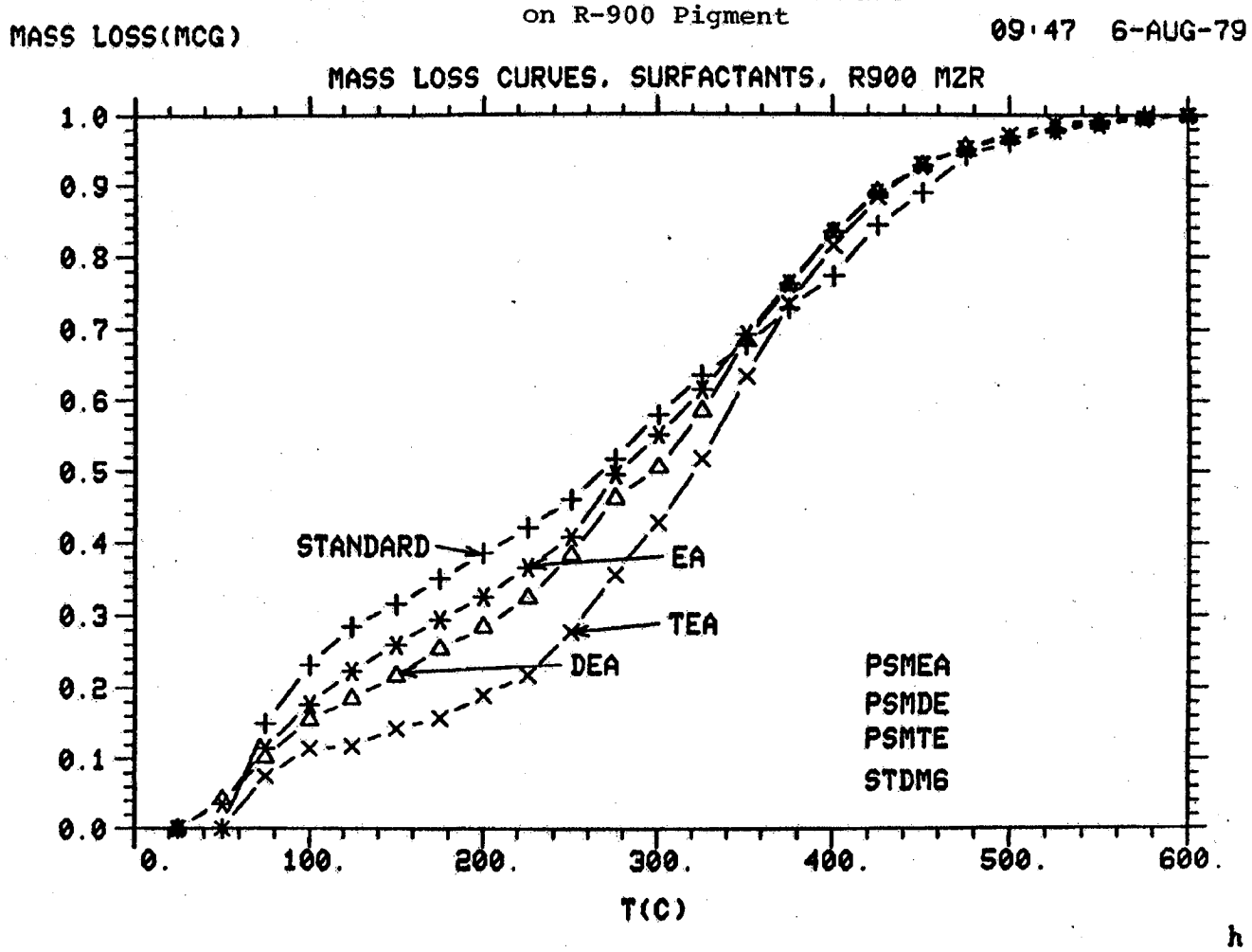


FIGURE IX

d (Mass Loss)/d (Temp.) vs. Temp. for R-900

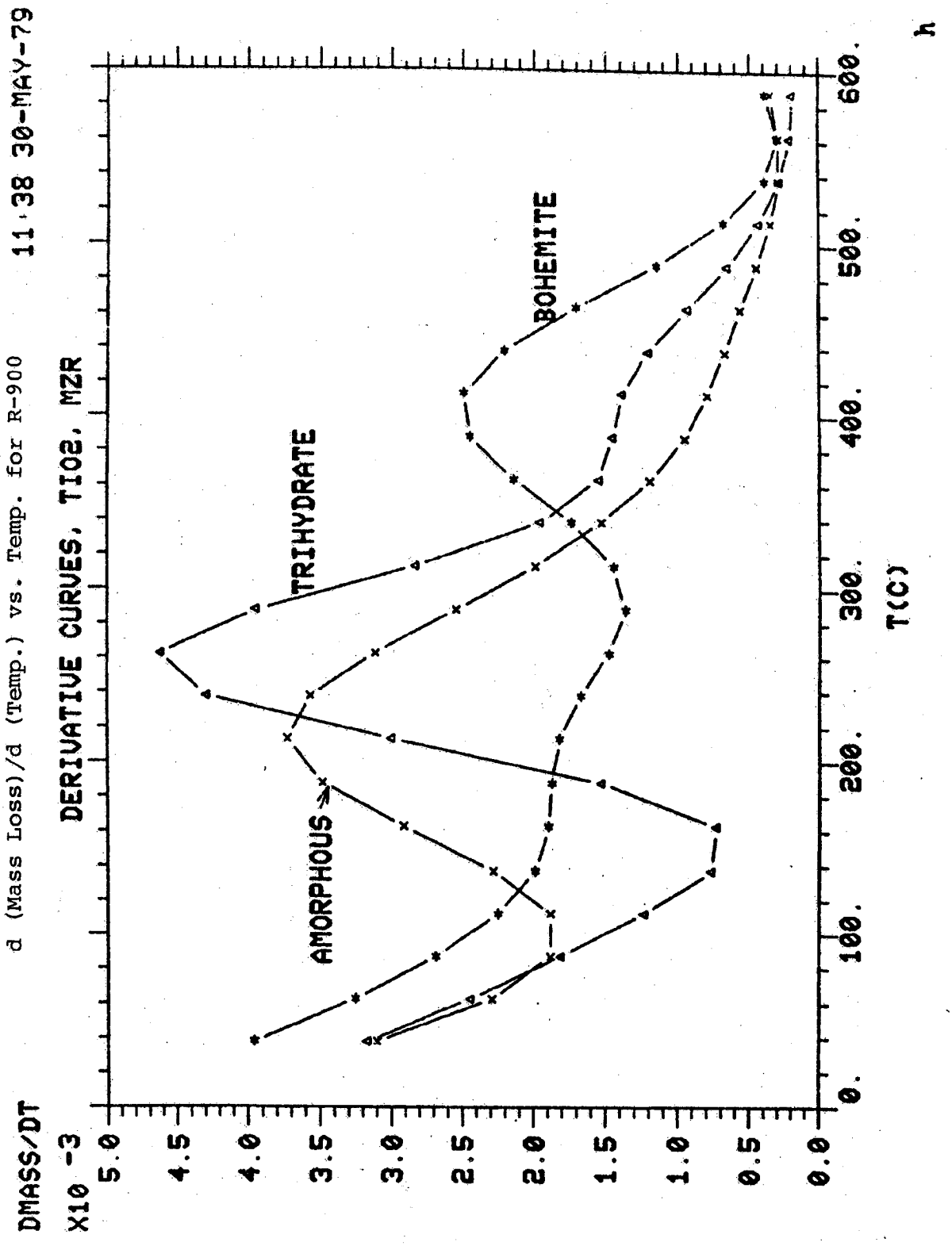


Figure X

TGA Mass Loss vs. Temperature
Um MZR TEA R-900

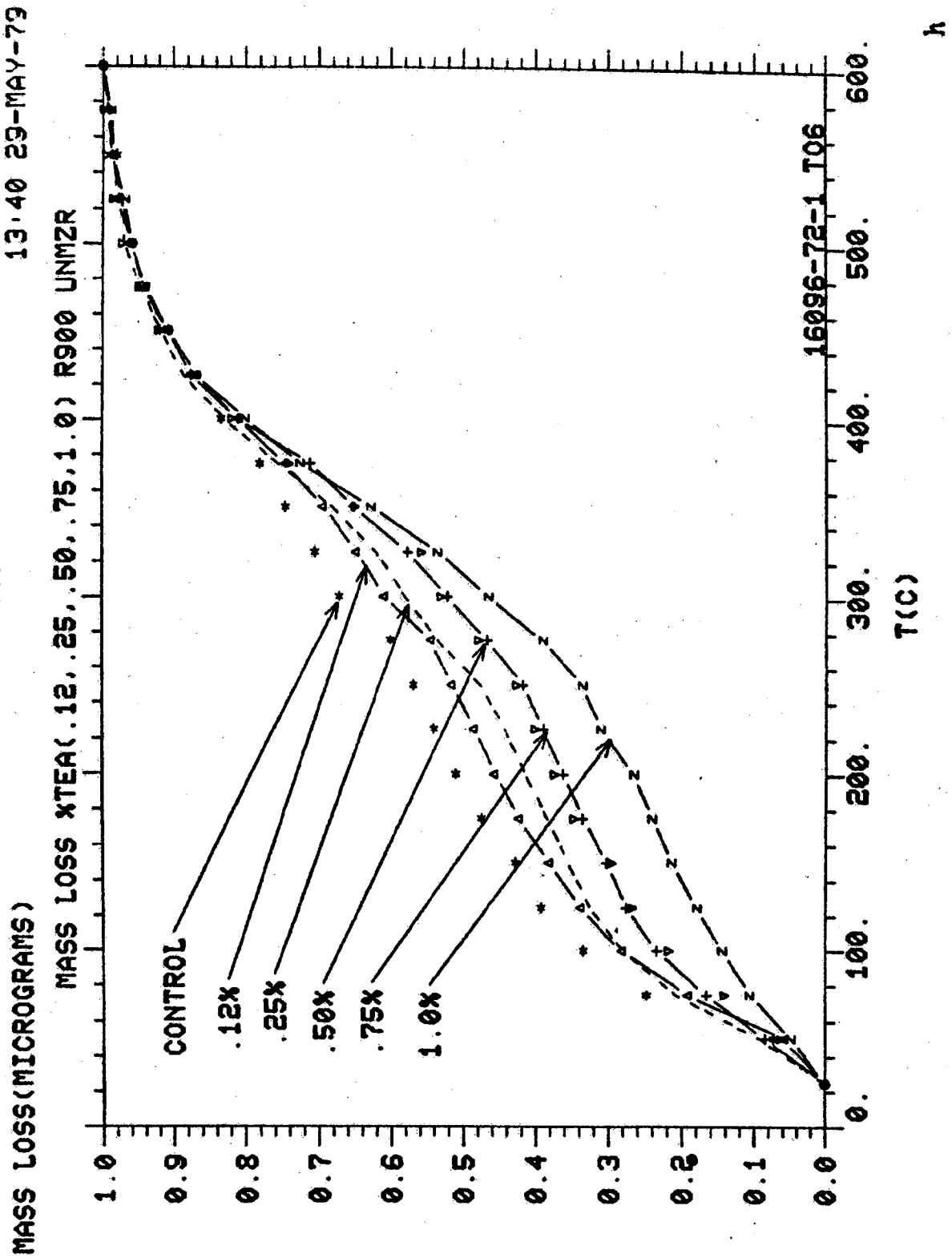
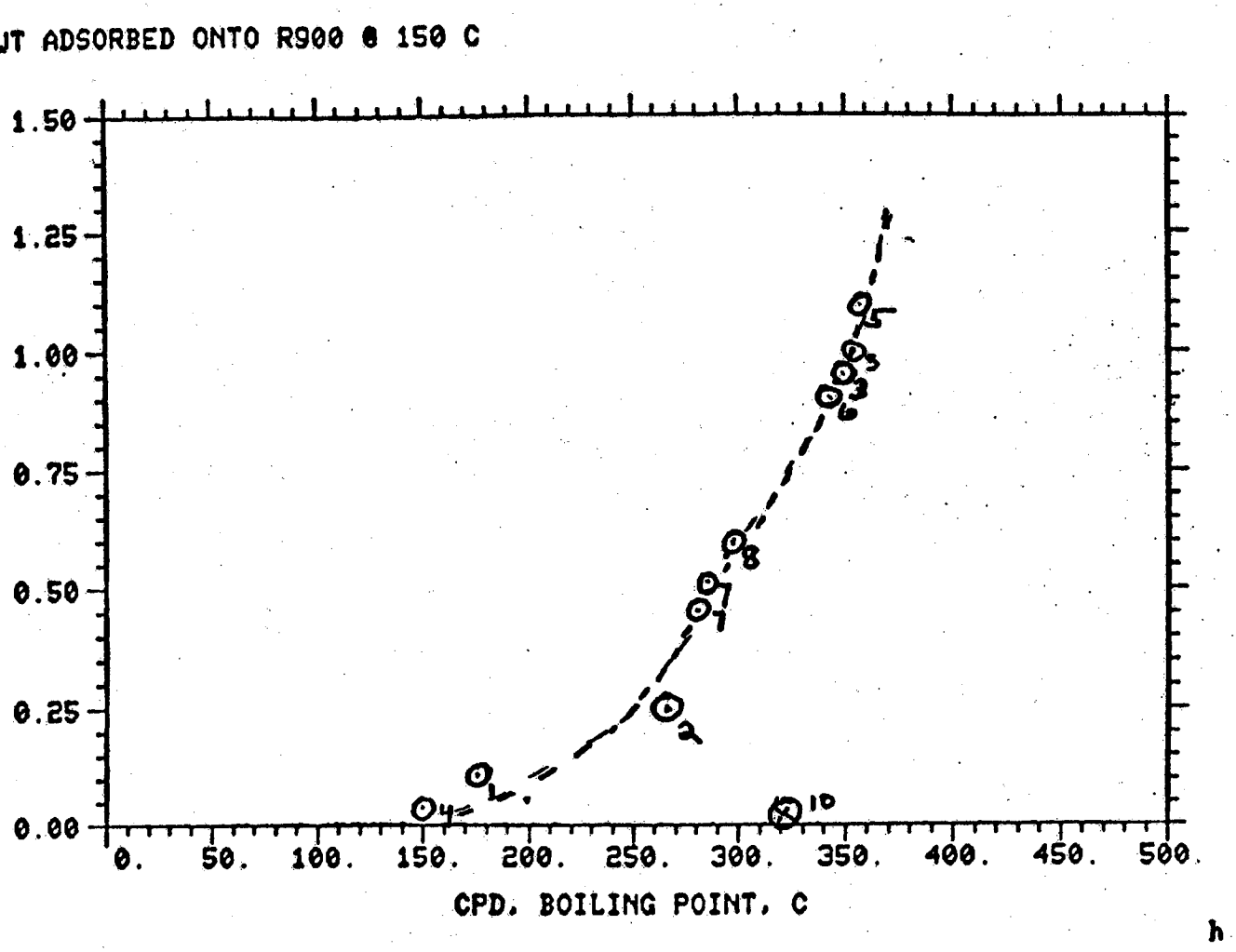


FIGURE XI

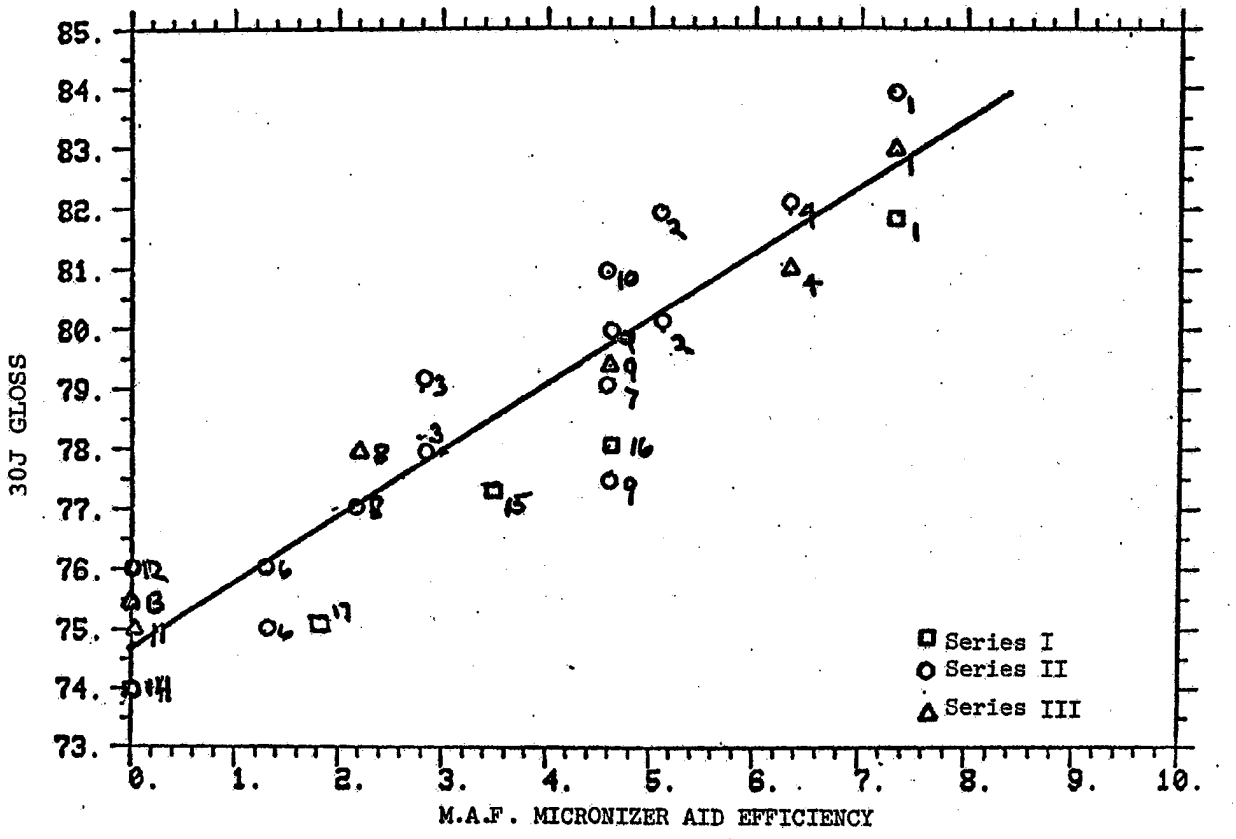
MICRONIZER AID BOILING POINT °C
VS
% WT. ADSORBED ONTO R-900 - 150°C



1) Ethanol Amine
2) Diethanol Amine
3) Triethanol Amine
4) AMP
5) Oleic Acid
6) Palmitic Acid
7) Trimethylol Propane
8) Glutaric Acid
9) Trimethylol Propane
10) Nona-decane

Figure XII

30J Gloss vs. Micronizer Aid Efficiency Factor



1. Tri-ethanol Amine
2. Di-ethanol Amine
3. Ethanol Amine
4. Trimethylol propane
6. Oleic acid
7. Adipic acid
8. Palmitic acid
9. Pimelic acid
10. Glutaric Acid
11. Nona-decane
12. Control (water)
13. Control (alcohol)
14. Control (hexane)
15. Amino-methyl propanol
16. Nitrilotriacetic acid
17. Di-octyl azelate

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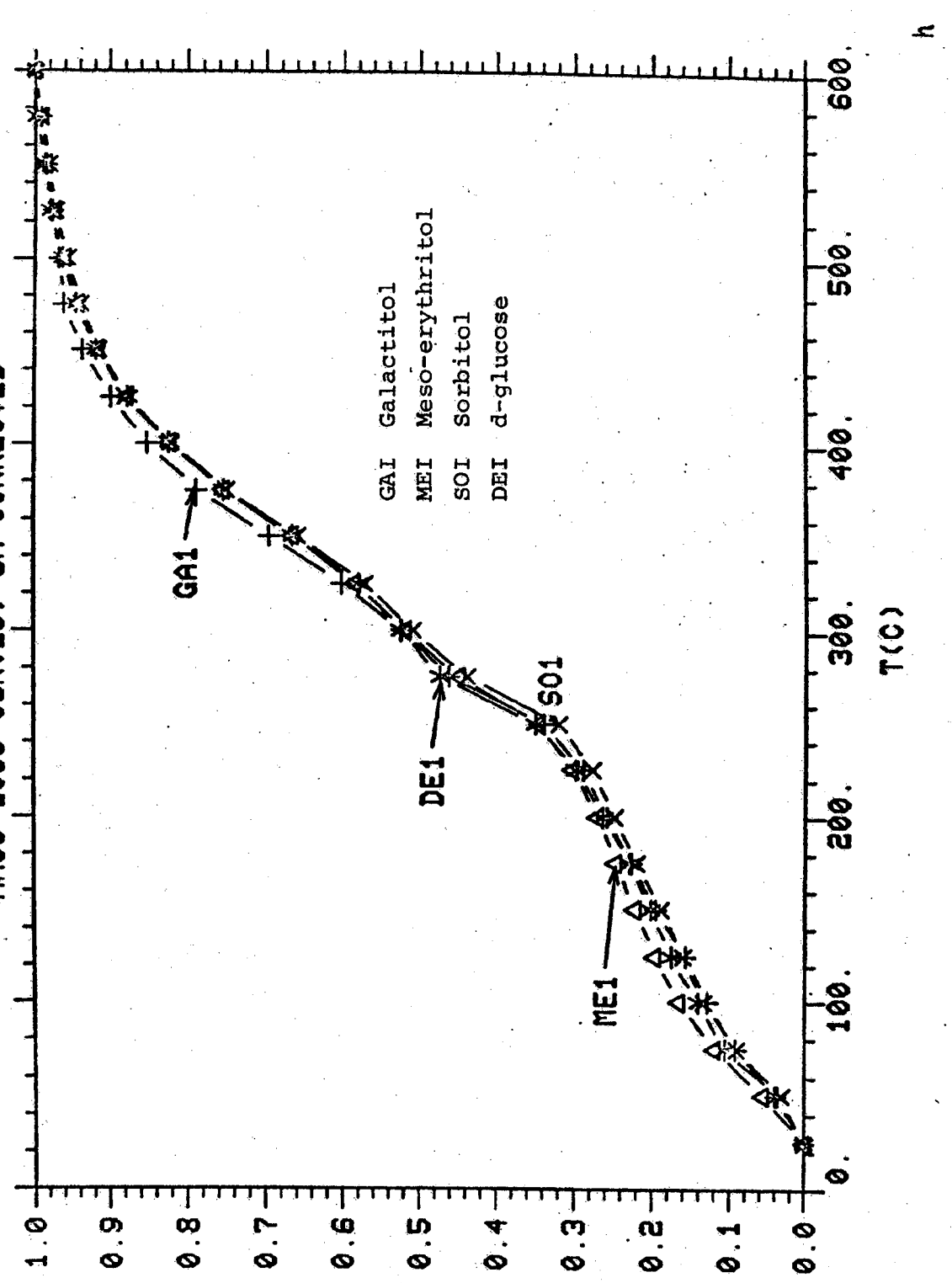

Figure XIII

TGA Mass Loss for Polyol
Treated R-900

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Figure XIV
Mass Loss for R-900 Treated
Sorbitol, TEA and Control

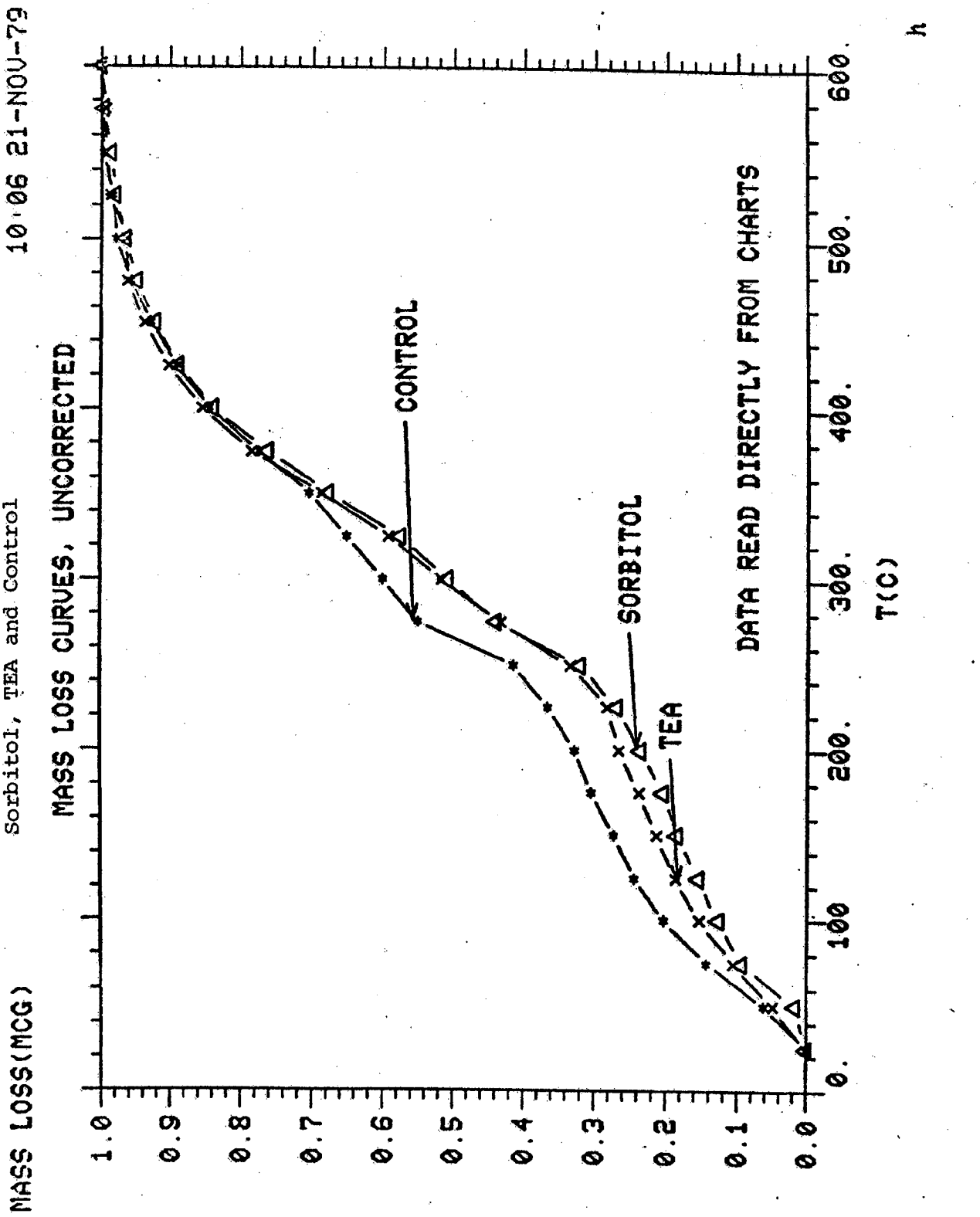

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Table I

Effect of TEA and S/P
ETC % Efficiency vs. TEA and S/P

% EFFICIENCY

Pigment Temp.	S/P	0.4	0.7	1.7	2.5	4.2
75°F	R-900 D.D.	20.4	23.9	29.0	15.2	11.0
	R-900 D.D. (TEA)	20.0	25.8	34.4	32.0	30.0
250°F	R-900 D.D.		24.0		10.0	
	R-900 D.D. (TEA)		26.0		28.0	
450°F	R-900 D.D.		15.0			
	R-900 D.D. (TEA)		26.0			
194°F	R-900 D.D.		26.0			14.0
20%RH	R-900 D.D.(TEA)		26.8			29.0

TABLE II

EDGE MOOR 8" MICRONIZER
30J GLOSS VS PIGMENT PRE-TREATMENT

Pigment Pre-treatment Temp.	S/P	1.5	2.3
75°F	R-900 DD	78	80
	R-900 DD (TEA)	78	84
250°F	R-900 DD	77	78
	R-900 DD (TEA)	78	815
450°F	R-900 DD	73	76
	R-900 DD (TEA)	78	815
200°F 20% RH	R-900 DD		78
	R-900 DD (TEA)		80

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TABLE III

TGA MICRONIZER AID ADSORPTION
BY TiO_2 PIGMENT

Micronizer Aid	TiO_2 Pigment	Temp. of Pigment °C	% wt. Adsorbed
Tri-ethanol Amine	Boehmite Al_2O_3 - R-900	150	0.98
	Trihydrate Al_2O_3 - R-900	150	0.43
	Amorphous Al_2O_3 - R-900	150	0.07
	/R-960	150	0.00
Tri-ethanol Amine	Boehmite Al_2O_3 - R-900	100	0.90
		150	0.91
		200	0.05
		250	0.00
Tri-ethanol Amine	Boehmite Al_2O_3 - R-900 First Heated to 600°C in Nitrogen	150	0.08

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TABLE IV

TGA MICRONIZER AID ADSORPTION
BY TiO_2 PIGMENT

Micronizer Aid	TiO_2 Pigment	Temp. of Pigment °C	% wt. Adsorbed
Ethanol amine	Boehmite Al_2O_3 - R-900	150	0.08
Diethanol amine	"	"	0.21
Triethanol amine	"	"	0.91
Oleic acid	"	"	1.16
Amino methyl propanol	"	"	0.00
Trimethylol propane	"	"	0.49
Palmitic acid	"	"	0.88
Glutaric Acid	"	"	0.57
Nona decane	"	"	0.00
Octo decane	"	"	0.00

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TABLE V

M.A.E. MICRONIZER AID EFFICIENCY, RATED

MICRONIZER AID	BOILING Pt. °C	MOLECULAR WEIGHT	'f' No. of FUNCTIONAL Groups	M.A.E. = (Boil. Pt. °C) ÷ (Mol. Wt) X 'f'
Pentaerythritol	381(1)	136	3(2)	8.40
Tri-ethanol Amine	360	149	3	7.24
Tri-methylol propane	280	1 4	3	6.27
Diethanol Amine	270[d]	105	2	5.14
Quadrol(4)	370	292	4(3)(3)	5.06 (3.80)
Adipic Acid	339	146	2	4.64
Nitrilo-Triacetic acid	240[d]	155	3	4.64
Glutaric Acid	303	132	2	4.60
Pimelic Acid	342	160	2	4.30
Amino-methyl propane	170	103	2	3.30
Ethanol amine	170	61	2	2.78
Di-octyl azelate	376	412	2	1.82
Palmitic acid	354	256	1	1.38
Oleic acid	360	282	1	1.27
Nona-decane	330	268	0	0.00
Octa-decane	310	254	0	0.00

(1) Boiling Point calculated from heat of vaporization
(2) Steric Hindrance of one Functional Group
(3) " " " two " Groups
(4) N,N,N'N' tetrakis (2-Hydroxy Propyl)ethylene diamine

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TABLE VI

RECIPROCAL FORMULA WEIGHTS FOR COMMON FUNCTIONAL GROUPS AND BOILING POINTS °C TO HAVE A GIVEN M.A.F.

FUNCTIONAL GROUP		RECIPROCAL FORMULA WEIGHT	B.P.°C FOR M.A.F. = 8	10
Amine	$>CH-NH_2$	1/29	232	290
Alcohol	$>C-OH$	1/30	240	300
Ketone	$>CH-\overset{O}{\overset{\|}{C}}-$	1/41	328	410
N-amine	$>CH-NH-CH_3$	1/43	344	430
Polyethylene oxide	$-CH_2-CH_2-O-$	1/44	352	440
Silicone	$-SiH_2-O-$	1/45	360	450
Ester	$CH-\overset{O}{\overset{\|}{C}}-O-$	1/57	456	570
Acid	$CH-\overset{O}{\overset{\|}{C}}-OH$	1/58	464	580
Modified Silicones	$-Si(CH_3)_2-O-$	1/74	592	740

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TABLE VII

NEW MICRONIZING AID CANDIDATES

Compound	Mol. Wt.	B.P °C	'f' No. of Funct. Groups	M.A.F.
d-glucose	180	310[d]	6	10.3
			5*	8.6
meso-erythritol	122	329	4	10.8
sorbitol	183	360[d]	5*	9.8
			4**	7.8
galactitol	183	360[s]	4**	7.8
TEA	149	360	3*	7.2

*assuming one group not functional

** " two groups " "

d, decomposes

s, sublimes

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TABLE VIII

30J GLOSS

ALTERNATIVES TO TEA

CANDIDATE	30J GLOSS*	COST CENTS/LB.
d-glucose**	75.7	13.0
m-erythritol	77.0	***
sorbitol	77.3	24.2
galactitol	76.0	***
TMP	77.7	27.5
TEA	76.7	16.0
Control	73	-

* S/P = 2.5, average of 3 measurements

** some decomposition during micronization

*** available only in small quantities

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LIST OF CHEMICALS

Chemical	Manufacturer/Distributor
d-Sorbitol	Fisher
meso-Erythritol	Aldrich
Dulcitol	Eastman
TMP	Aldrich
Dextrose	Fisher
Carbowax 200	Union Carbide
" 300	" "
Palmetic Acid	Fisher
Ethanol Amine	Eastman
Calcium Nitrate	MCB
Sodium Silicate	Du Pont
TEA	Fisher
Boric Acid	Fisher
Glutaric Acid	Eastman
Dioctyl Azelate	Reichhold
Nona-Decane	Aldrich
Sodium Borate	Fisher
1,2,4 Butanetrol	Aldrich
Adipic Acid	Fisher
Nitrilo Acetic Acid	Eastman
Pimelic Acid	"
Pentaerythritol	"
Oleic Acid	Fisher
Sodium Pyro Phosphate	"
" Metaborate	"
TEA	"
UPLA 713	Henkle
774	"
801	"
734	"
803	"
2-Amino-2 Methyl-/Propanol	Aldrich
TKPP	Alfa

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