**GEORGIA INSTITUTE OF TECHNOLOGY**
OFFICE OF CONTRACT ADMINISTRATION
**SPONSORED PROJECT INITIATION**

Date: 10-30-79

Project Title: Activated Carbon Sample Analyses

Project No: A-2467

Project Director: Dr. Stanton B. Smith

Sponsor: Shirco, Inc; Dallas, Texas 75207

Agreement Period: From 8/30/79 Until 10/15/79

Type Agreement: Purchase Order No. 238-3656, dated 8/30/79

Amount: Not to exceed $1,050

Reports Required: None specified

Sponsor Contact Person (s):

Technical Matters

Dr. F.K. McGinnis, III
Shirco, Inc.
2451 Stemmons Freeway
Dallas, Texas 75207

Contractual Matters
(thru OCA)

Mr. Ken Slaton
Shirco, Inc.
2451 Stemmons Freeway
Dallas, Texas 75207
(214) 630-7511

Defense Priority Rating:

Assigned to: CMSL/CEB (School/Laboratory)

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GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

# SPONSORED PROJECT TERMINATION SHEET

Date 10/2/81

Project Title: Activated Carbon Sample Analyses

Project No: A-2467

Project Director: Dr. Stanton B. Smith

Sponsor: Shirco, Inc.; Dallas, Texas

Effective Termination Date: 9/30/81

Clearance of Accounting Charges: 9/30/81

Grant/Contract Closeout Actions Remaining:

- [x] Final Invoice and Closing Documents
- [ ] Final Fiscal Report
- [ ] Final Report of Inventions
- [ ] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other _____

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FORM OCA 10:781

ENGINEERING EXPERIMENT STATION
GEORGIA INSTITUTE OF TECHNOLOGY • ATLANTA, GEORGIA 30332

October 2, 1980

ref: A 2467

Dr. F. K. McGinnis,
Executive Vice President
Shirco, Inc.
2451 Stemmons Freeway
Dallas, Texas 15207

Dear Mac:

The attached data should adequately cover the evaluation of the third cycle regeneration. I think you will be pleased with our findings in that there appears to have been very little change in the carbon over this third period of exposure and thermal regeneration.

As in the case of the second regeneration, we calcined the spent sample so as to remove volatile matter before attempting to do the pore-size distribution curve by nitrogen adsorption. Since it appeared that the calcining method used in the previous set of samples was too long resulting in some shrinkage, I used a somewhat different procedure. A fifty gram portion of the granular carbon was quickly poured into the inclined rotary furnace already set at 1500°F (816°C). Heating was continued while the furnace was rotated and a stream of nitrogen run over the sample for thirty minutes. The calcined material was then quickly dropped into the cooling tube without exposure to external air and rapidly cooled. The density of the recovered calcined material is given in the tabular data. (This density was determined on a somewhat smaller amount of material than the specified 100 ml sample.) I think this procedure was somewhat better than the previous as there was a slight decrease in density upon calcination rather than an increase as in the previous cycle.

There is one change which may be significant and that is the greater reduction in mean particle diameter. In the second cycle, a reduction of 5% took place, but in the third cycle there appears to be about a 16% reduction. Since the carbon appeared to have the same abrasion resistance as in the previous cycles, possibly there has been greater stress applied in the handling of the spent or recycled carbon. It might be well to investigate the condition of the transfer system.

I believe the rest of the report speaks for itself. I regret that we were not able to get the results back to you within the one-month target date but vacations which were already scheduled caused some delay in the processing of the samples.

Thank you for submitting the samples from the third cycle. We will be looking forward to receiving further samples after the fourth cycle of regeneration has been completed. With this reporting completed, we will be sending an invoice amounting to $1200.00.

Thank you for continuing with this program.

Very truly yours,

Stanton B. Smith, Ph.D
Principle Research Scientist

SBS:mla

ENGINEERING EXPERIMENT STATION
GEORGIA INSTITUTE OF TECHNOLOGY • ATLANTA, GEORGIA 30332

REPORT TO SHIRCO, INC.

EVALUATION OF THIRD CYCLE REGENERATED CARBON, HD1030
FROM EVANSVILLE, INDIANA

Project No.: A-2467

GENERAL COMMENTS

The results of physical and chemical tests on the "Third Cycle Regenerated" carbon, the "Third Cycle Feed" (Spent) carbon, and the laboratory "Calcined Spent" carbon, when compared with data from the "Regenerated Second Cycle" sample indicate that a very efficient regeneration has been accomplished. As in the previous cycle there is evidence of very little pickup of organic matter during the adsorption cycle with the volatile content increased only about 4.5% or 2.2 g per 100 ml on a volume basis. There was, however, evidence of some saturation, particularly in the Modified Phenol Value (MPV) and to a lesser extent in Molasses Decolorizing Index. The regeneration was very effective as indicated by an increase in Iodine Number over the previous regeneration on both a weight and volume basis. The MPV's indicated a slight improvement on a volume basis over the previous cycle. Also, the Decolorizing Index, although somewhat lower on a weight basis, is nevertheless essentially restored on an equal volume comparison. The Ash Content has increased slightly over the second cycle but the difference is not thought to be significant. The Apparent Density has increased almost 10% above the previous regeneration but this is probably due to a change in particle size distribution as evidenced by a reduced Mean Particle Diameter upon regeneration; rather than due to failure to burn off the carbonized adsorbed layer.

The Nitrogen Adsorption data are very similar for the three samples. The BET Areas were increased in the Regenerated Third Cycle material almost in exact proportion to the iodine numbers. This is a good indication, showing that both the small and large pores are being opened up and maintained so that there is unlikely to be any gradual degradation of adsorptive power as cycles are repeated. The trend of a continued slight increase in adsorptive power is borne out by the Pore-size Distribution curves shown

in Figure 1. The Third Cycle Regenerated sample appears to have slightly less surface area in pores greater than two hundred Angstrom units diameter, but this is probably of little consequence. The pore-size distributions below 200 Angstroms for the Second Cycle Regenerated carbon, Calcined Spent carbon and Third Cycle Regenerated carbon are so parallel to one another that no significant differences can be noted.

In summary then, it appears that the third cycle was carried out very successfully under conditions of regeneration which have been skillfully adjusted to the small degree of pickup of organic matter in the adsorption cycle. Though there has been a slight reduction in Particle Diameter, the hardness of the original has been maintained and, if additions of fresh carbon are made to make up for attrition losses, the physical and adsorptive properties of the carbon charge should be maintained at an essentially constant level.

**TABLE 1**

SHIRCO INC., THIRD CYCLE REGENERATION OF HD 1030 ACTIVATED CARBON

**SUMMARY TABLE**

| PROPERTY | Sample: | REGENERATED 2nd Cycle by weight | (by vol.)* | SPENT 3rd Cycle by weight | (by vol.) | REGENERATED 3rd Cycle by weight | (by vol.) |
|---|---|---|---|---|---|---|---|
| BET Surface Area | $m^2/g$ | 644 | | 655.6 - Calcined Sample | | 668.0 | |
| | $m^2/ml$ | | (260) | | (274.0) | | (293.9) |
| Iodine No. | mg/g | 596 | | 467 | | 650 | |
| | mg/ml | | (240) | | (204) | | (286) |
| Modified Phenol Value (Westvaco Meth.) | ppm | 28.5 | | 61.8 | | 30.4 | |
| | ml C/$10^6$g** | | (70.7) | | (139.5) | | (69.1) |
| (AWWA Calc. Meth) | mg/lsol'n | 3.25 | | 7.05 | | 3.46 | |
| | ul C/lsol'n** | | (8.06) | | (15.91) | | (7.86) |
| Molasses Decolorizing Index | DI Units | 14.7 | | 10.4 | | 13.7 | |
| | DIU/ml | | (5.92) | | (4.61) | | (6.03) |
| Moisture w.b. | % | 57.0 | | 5.54 | | 51.5 | |
| | g/100ml | | (23.0) | | (2.45) | | (22.7) |
| Ash | % | 15.7 | | 16.5 | | 17.9 | |
| | g/100ml | | (6.33) | | (7.31) | | (7.88) |
| Volatile Matter | % | 6.6 | | 11.0 | | 6.1 | |
| | g/100ml | | (2.66) | | (4.87) | | (2.68) |
| Apparent Density | g/ml | .403 | | .443 (.418 Calcined) | | .440 | |

| Screen Analysis | | REGENERATED 2nd Cycle | SPENT 3rd Cyc. | REGENERATED 3rd Cycle |
|---|---|---|---|---|
| U.S. Mesh 0 n 10 | % | .1 | 0 | 0 |
| 10 x 12 | % | 1.9 | 1.4 | 1.0 |
| 12 x 16 | % | 37.8 | 31.6 | 19.2 |
| 16 x 20 | % | 43.0 | 44.0 | 40.4 |
| 20 x 30 | % | 13.1 | 18.5 | 26.4 |
| 30 x 40 | % | 2.5 | 3.6 | 8.6 |
| Through 40 | % | 1.6 | 0.9 | 4.4 |
| | | 100.0 | 100.0 | 100.0 |
| Particle Diameter (calculated) Mean | mm | 1.12 | 1.076 | .937 |
| (from graph) Median | mm | 1.10 | 1.05 | .91 |
| Abrasion Number | % by mean pd | 50.7 | 47.7 | 50.0 |
| | % by median pd | 53.6 | 50.5 | 56.0 |

* Values in ( ) calculated by multiplying by the App. Density
** Values in ( ) calculated by dividing by the App. Density

## DETAILED EVALUATION

(Refer to Table 1 for Numerical Data)

The BET Surface Areas show that the carbon has been completely regenerated and, in fact, increased in total area above the Virgin* material and Second Cycle Regenerated* carbon. This is true on both the weight and volume bases. The Third Cycle Feed (Spent) sample may be somewhat inconsistent but it must be remembered that this determination was done on a sample calcined at 1500°C for one half hour. This treatment is apparently a good way of regenerating even though no oxygen was admitted intentionally to the system. There is, however, an area increase in the Third Cycle Regenerated sample above this figure. The fact that the Spent Third Cycle sample is above the Regenerated Second Cycle may be due to sampling differences in the two materials.

The Iodine Numbers show that the regeneration in the third cycle was very effective and a higher value was reached on both a weight and volume basis than in the second cycle. The Spent material, which in this case, was not calcined shows the effect of partial saturation with organic matter and particularly indicates a higher degree of saturation on a volume basis. However, there is still considerable active surface remaining in the carbon after use indicating that it could probably be left on stream for a longer time and still be quite effective.

The Modified Phenol Values indicate that there was considerable saturation of the finer pores as shown by the higher MPV value for the Spent sample. However, most of these pores were again opened up in the regeneration so that a high degree of activity for removing small molecules has been regained. As a matter of fact, on a volume basis, the Third Cycle Regenerated material is slightly better than the Regenerated Second Cycle sample. In comparing the Modified Phenol Values, it must be remembered that they are expressed on a reciprocal basis and the lower the number, the better the carbon.

The Molasses Decolorizing Index shows that the area in the large pores which accept the large molasses color bodies have been sufficiently opened up and though the Third Cycle Regeneration appears lower on a weight basis than the Second Cycle Regenerated sample, the density difference makes up for this and when the volume basis figures are considered a net

* Data taken from previous report.

increase in decolorizing power is noted. The Spent sample indicates some impairment of the surface by adsorbed materials but to nearly the same extent as shown by the MPV. It may thus be inferred that the saturation effect has been greater in respect to small molecules than for large.

The Moisture results on a wet basis are not particularly significant but indicate only that the degree of drainage in the very wet samples is about the same in third cycle as in the second. In fact, on a volume basis, which is the more correct comparison, the values are identical within experimental sampling limits. The Spent sample was already dried so that it cannot be included in the comparison of the drained carbon samples.

The Ash results indicate that there has been a slight increase over the third cycle on a volume basis. About 1 g/100 ml seems to have been picked up in the contact with the raw water and on regeneration this amount is increased slightly probably due to the shrinkage effect. This amount of ash pickup should be no cause for concern unless a trend continues for a number of cycles.

Volatile Matter results show that the Spent carbon has a moderate increase over the Second Cycle Regenerated sample but again the indication is that the carbon was not very highly saturated before being regenerated. The Volatile Matter then returned to almost the identical level in the previous cycle. This particular test does not reproduce as well as some of the other methods so that the difference of about .5% is not regarded as significant. In any case, on a volume basis, the Second and Third Cycle volatile contents are identical.

Apparent Density values indicate an almost 10% increase over the Second Cycle Regeneration. This is difficult to explain since the regeneration appeared to be thorough and there was only a slight increase in ash on a volume basis. The Spent sample is not as high as one would expect from the increased volatiles content. There was an expected reduction in Apparent Density upon calcining of the Spent sample and one would expect the Regenerated Third Cycle to be even somewhat lower than this value of .418. However, two things have probably taken place in the regeneration: (1) there is some shrinkage and (2) a rather pronounced change in the particle-size distribution. The shift to finer particle

sizes could easily explain the increase in density of roughly 5%.

Particle Size measurements as shown by the screen analyses of the three samples indicate very little change from the Regenerated Second Cycle material to the Third Cycle Spent sample. However, the Third Cycle Regenerated sample indicates a marked change in particle size with a sizable drop in the 10 through 20 mesh fractions. The Mean Particle Diameters and the Median Particle Diameters show essentially the same thing; that there has been a slight drop in size between the Second Cycle Regenerated and the Spent material, but a rahter large drop for the Third Cycle Regenerated carbon. There appears to have been some attrition during the regeneration and some accumulation of fines in the process.

In Abrasion Number data is encouraging in that in spite of the change in Mean Particle Diameter the hardness, as indicated by abrasion resistance, remains about the same in the third cycle as in the second. As a matter of fact, if the Median Particle Diameters are used, there appears to be a slight increase on the third cycle. The fact that the Spent sample gives somewhat lower values than the Regenerated is probably not significant but may indicate the wearing away of some material collected on the surface which may be sloughed off in the test.

Pore-Size Distribution curves as shown in Figure 1 indicate very small differences in all three samples. For all practical purposes, the pore sizes of the three samples may be considered identical. To attempt to differentiate these curves would probably be misconstruing the accuracy of the data or the validity of the sampling. In the absence of any observable changes, one can say that the regeneration has been complete and the carbon is restored to the pore distribution of the previous cycle.

FIGURE 1

CUMULATIVE SURFACE AREA DISTRIBUTION

SHIRCO, INC. (Evansville, 3rd Cyc.)

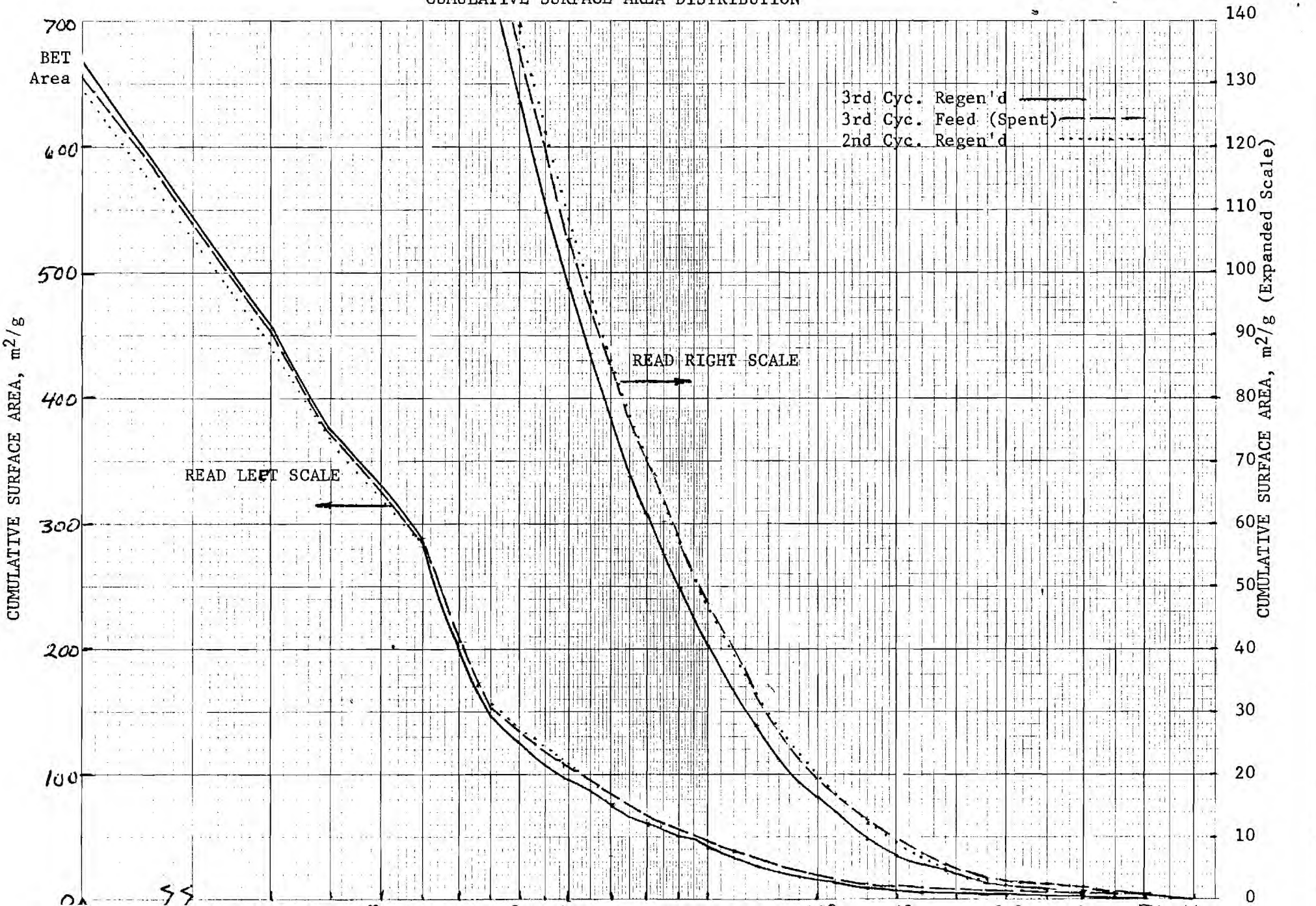


FIGURE 2

PARTICLE SIZE DISTRIBUTION

SHIRCO, INC. (3rd Cyc. Feed (Spent))
Evansville, IN

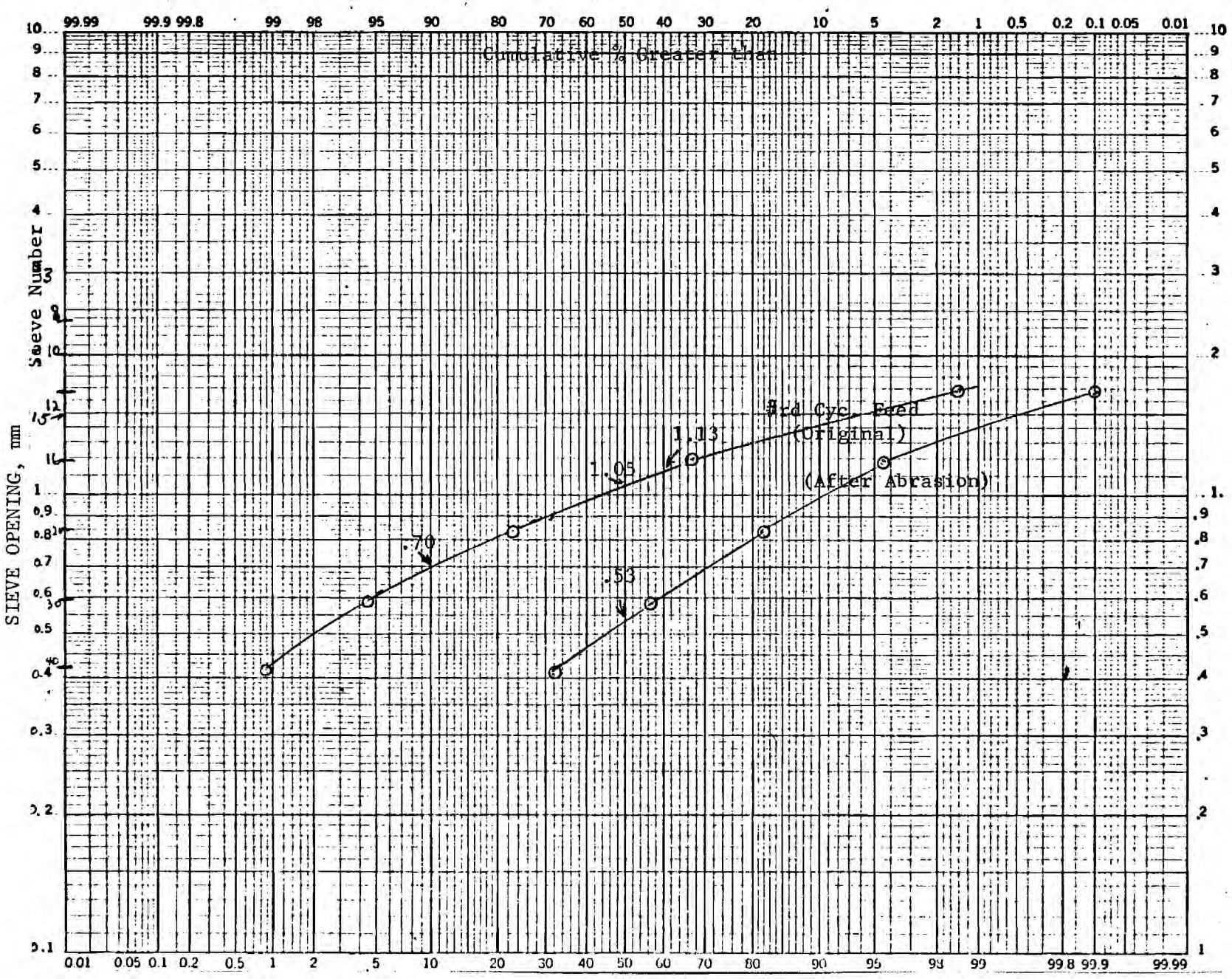


FIGURE 3

PARTICLE SIZE DISTRIBUTION

SHIRCO, INC. (3rd Cyc. Regenerated)
Evansville, IN

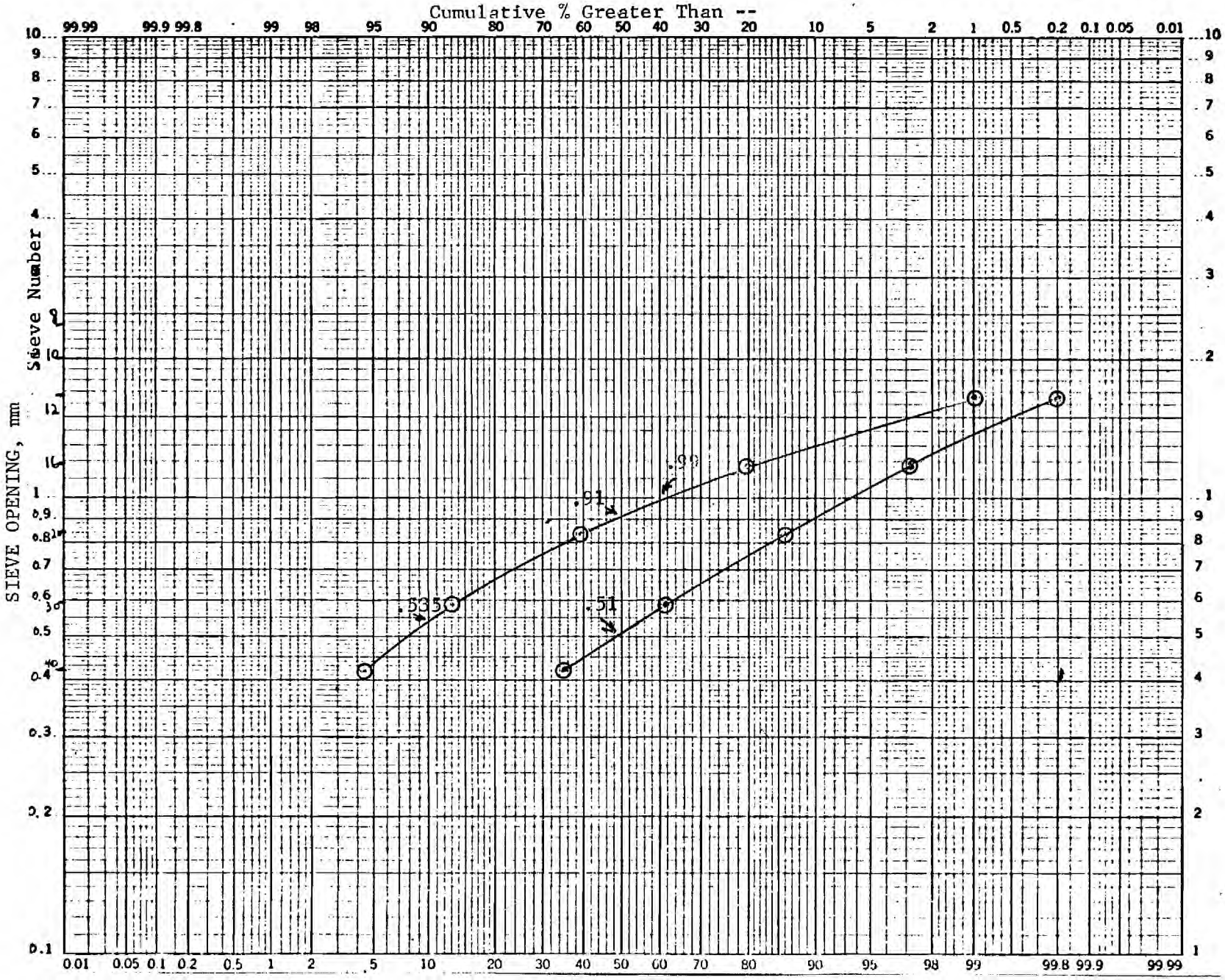
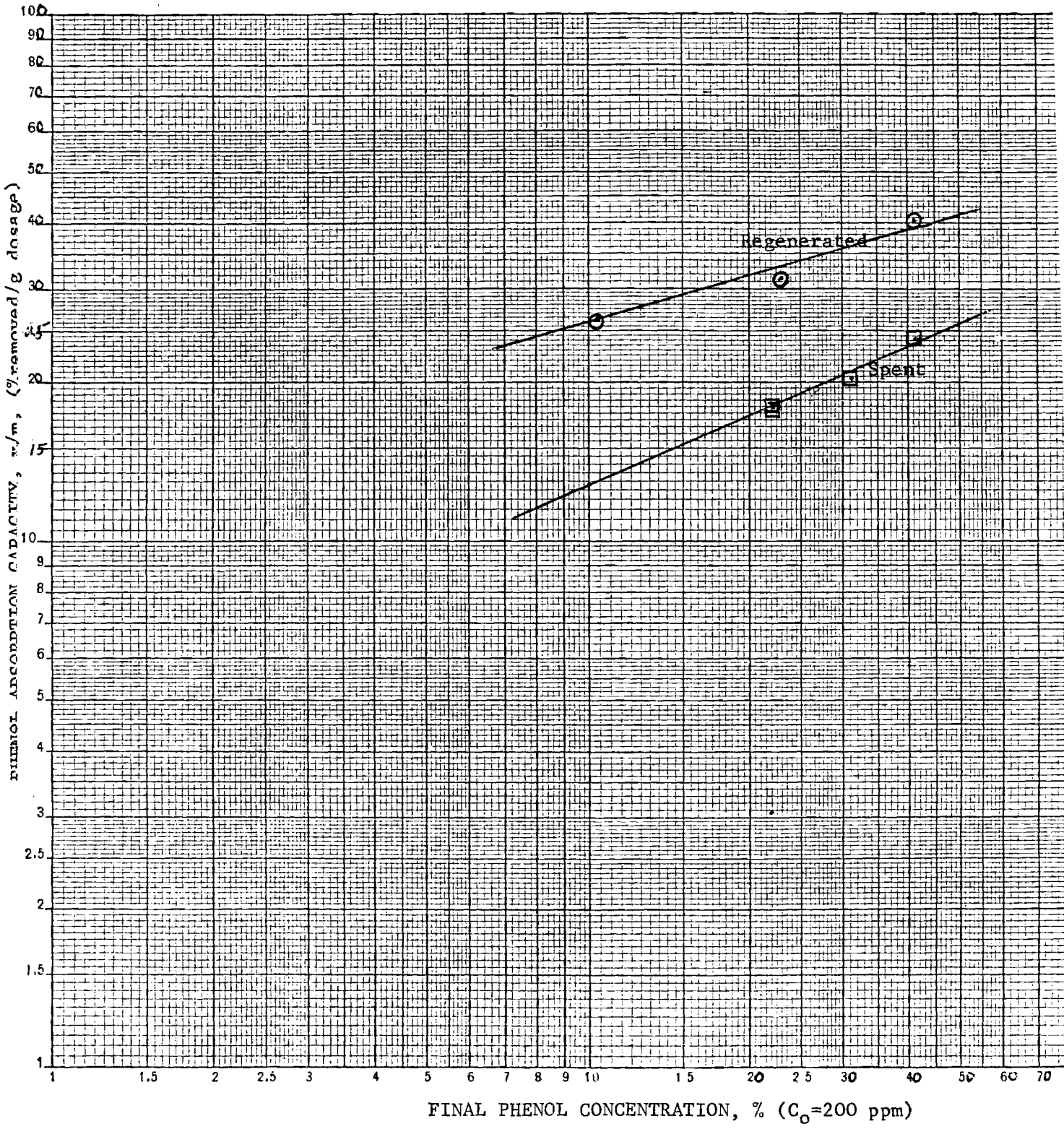


FIGURE 4

SHIRCO, INC. (Evansville, 3rd Cyc

PHENOL ISOTHERMS
for MPV Determinations



ENGINEERING EXPERIMENT STATION
GEORGIA INSTITUTE OF TECHNOLOGY • ATLANTA, GEORGIA 30332

# CARBON ANALYSIS REPORT

SAMPLE:

Source: SHIRCO, INC. (Rec'd 8/18/80) **Grade (if known):** DARCO HD1030

Designation: Cycle 3, Feed (Evansville, IN) (Spent Sample)

Project No.: A-2467

ANALYTICAL RESULTS (by Westvaco Standard Methods unless otherwise noted)

| TEST | Units | RESULTS Replicates (1) | (2) | Average |
|---|---|---|---|---|
| Abrasion No. (Ro-Tap) | % | 47.7 | | |
| * Iodine No. | mg/g | 460 | 462 | 461 |
| Surface Area, BET $N_2$ (1) | $m^2/g$ | (655.6 on Calcined Sample) | | |
| *Molasses Decolorizing Index | - | 9.8 | 10.9 | 10.4 |
| Moisture, w.b. | % | 5.22 | 5.86 | 5.54 |
| *Volatile Matter, d.b. | % | 11.0 | 11.0 | 11.0 |
| *Ash, Total | % | 16.5 | 16.4 | 16.5 |
| Particle Size (U.S. Sieve #) | nominal | 10 X 30 | | |
| Oversize (10) | % | 0 | | |
| Undersize (30) | % | 4.5 | | |
| Effective Size (10% smaller than) | mm | .70 | | |
| Uniformity Coefficient (60%/10%) | | 1.61 | | |
| Mean Particle Diameter (Calc'd) | mm | 1.076 | | |
| Median Particle Diam. (Graph 50%) | mm | 1.05 | | |
| Apparent Density | g/ml | .443* | .442* | .443* .417 .419 .418Ca Sa |
| *Modified Phenol Value, MPV | | | | |
| Westvaco method, 790 Const. | ppm | 61.8 | | |
| AWWA B600-78, 90 Const. | g/l | 7.05 | | |

NOTES AND REMARKS:

(1) Micromeritics automated method, Performed on sample calcined at 1500°F, 30 mi
*Values corrected for moisture in dried sample.

Signed: _____
Stanton B. Smith, Ph.D.
Principal Research Scientist

ENGINEERING EXPERIMENT STATION
GEORGIA INSTITUTE OF TECHNOLOGY • ATLANTA, GEORGIA 30332

# CARBON ANALYSIS REPORT

SAMPLE:

Source: SHIRCO, INC. (Rec'd 8/18/80) Grade (if known): DARCO HD1030

Designation: Cycle 3, Regenerated (Evansville, IN)

Project No.: A-2467

ANALYTICAL RESULTS (by Westvaco Standard Methods unless otherwise noted)

| TEST | Units | RESULTS Replicates (1) | (2) | Average |
|---|---|---|---|---|
| Abrasion No. (Ro-Tap) | % | 50.0 | | |
| *Iodine No. | mg/g | 650 | 650 | 650 |
| Surface Area, BET $N_2$ (1) | $m^2/g$ | 668.0 | | |
| *Molasses Decolorizing Index | - | 14.1 | 13.3 | 13.7 |
| Moisture, w.b. | % | 51.2 | 51.8 | 51.5 |
| *Volatile Matter, d.b. | % | 6.9 | 5.2 | 6.1 |
| *Ash, Total | % | 17.9 | 17.9 | 17.9 |
| Particle Size (U.S. Sieve #) | nominal | 10 X 30 | | |
| Oversize (10) | % | 0 | | |
| Undersize (30) | % | 13.0 | | |
| Effective Size (10% smaller than) | mm | .535 | | |
| Uniformity Coefficient (60%/10%) | | 1.85 | | |
| Mean Particle Diameter (Calc'd) | mm | .937 | | |
| Median Particle Diam. (Graph 50%) | mm | .91 | | |
| *Apparent Density | g/ml | .440 | .440 | .440 |
| *Modified Phenol Value, MPV | | | | |
| Westvaco method, 790 Const. | ppm | 30.4 | | |
| AWWA B600-78, 90 Const. | g/l | 3.46 | | |

NOTES AND REMARKS:

(1) Micromeritics automated method

* Values corrected for moisture in dried sample

Signed: _____

Stanton B. Smith, Ph.D.
Principal Research Scientist