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**SPECIFICATION DEVELOPMENT
FOR A VISCOELASTIC POLYMER ADDITIVE
BASED ON CORRELATIONS
BETWEEN PERFORMANCE CRITERIA AND
MATERIAL CHARACTERIZATION TESTS**

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December 1989

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PREFACE

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SPECIFICATION DEVELOPMENT FOR A VISCOELASTIC POLYMER ADDITIVE
BASED ON CORRELATIONS BETWEEN
PERFORMANCE CRITERIA AND MATERIAL CHARACTERIZATION TESTS

1. INTRODUCTION

1.1 Rationale

Either performance or material property tests could be used for the QA/QC surveillance of a viscoelastic polymer additive (VEPA) for the Fluid Dynamics program. Performance tests are usually preferred, however, the end-use performance test could require expensive fluid dynamics trials. A second performance test choice would be chamber tests correlated to the fluid performance tests based on developmental testing. Again, these tests are prohibitively expensive and have turnaround times that are too long to be useful. Both of these might be characterized as the "Test-to-Buy" methods.

Laboratory tests correlated to field and chamber tests are a third performance test category. For example, rheological measurements of viscoelastic properties are feasible for QA/QC. In addition, rheological property measurements are already programmed as the method for adjusting VEPA concentration to compensate for batch fluctuations in molecular weight (MW) and/or compositional parameters, if a single batch blend cannot be processed.

Material tests are not preferred compared to performance tests; however, the nature of the VEPA end-use requires the consideration of supplemental material tests. Material tests can be either the preferred tests of procedure independent intrinsic properties that are directly related to performance or tests of secondary properties that have some indirect relation to performance and are procedure dependent. In order to design intrinsic tests, the cause and effect relation between property and performance must be known. Due to the complexity of molecular level viscoelastic processes, the intrinsic property can only be hypothesized to involve transient entanglement in the semi-dilute regime; both energetic/mechanical and entropic processes can be targets for intrinsic property measurement.

1.2 Selection of Sample State and Test Solvents

Also involved in the material tests are the physical state of the VEPA. In other words, the stage of the process in which the tests should be carried out to obtain the intrinsic properties of the sample has to be determined. For example, the aliquots of the emulsion system as well as the dried polymer powder can be used for the material tests. This is important since the exact sample forms are relevant to specific material tests, and thus to specific performance criteria.

The performance criteria such as dissolution process/kinetics and stability of the resulting solution can be indirectly obtained from some of the material tests or measured directly. Since these properties depend on not only the VEPA but also the solvent system, the selection of model solvent system(s) should be based on direct experimental comparisons.

2. EVALUATION

2.1 Performance Criteria

A preliminary evaluation of performance criteria suggests the following categories:

1. Fluid dynamic viscoelastic performance (Rheometrics Fluid Rheometer and Magnetic Sphere Rheometer).

2. Processing performance of emulsion batch blending homogeneity. Candidate methods are:

a) Well-characterized, small batch emulsion blending homogeneity vs blending homogeneity of the scale-up,

b) Mathematical sum of experimental data for each batch vs experimental data for the emulsion blend, and

c) Deviation of the emulsion blend from the dried polymer blend.

3. Processing performance concerning dissolution time vs viscosity, MW, MW distribution (MWD), etc.

4. Surveillance of stability in storage; storage time vs solution viscosity (Magnetic Sphere Rheometer), MW, MWD, gel fraction, etc.

2.2 Evaluation Methodology

In the absence of a complete understanding of the intrinsic properties controlling performance, additional tests for secondary, procedure dependent properties might be required. These properties are the usual characterization methods designed for specifications. A continuation of the approach initiated above might include the following steps.

1. Identify each critical performance criterion.

2. Evaluate the intrinsic property controlling performance for each criterion.

3. Identify candidate tests for each intrinsic property.

4. Identify candidate secondary or supporting tests for each intrinsic property.

5. Integrate all of the performance/property/test requirements, if they overlap.

6. Develop an experimental design and experimental approach.

7. Based on incremental results obtained, modify the experimental design by interaction among:

- a) the developers (CRDEC and MTL),
- b) the scale-up contractor (Lehigh University),
- c) ARO investigators with related expertise (SUNY at Stonybrook), and
- d) characterization collaborators (I.C.S., Strasbourg).

2.3 Physical State of VEPA

There are at least 4 sample physical states or formulations of interest (Table 1). Specific sample forms are relevant to specific performance criteria, as listed in Table 2.

Whenever possible, specifications employing hazardous products will be replaced by correlated tests in the solvent mixture and/or model liquid systems.

Table 1. Physical State of VEPA and Code Used for Each State.

<u>Code</u>	<u>Sample Formulation or Physical State</u>
P	Polymer solution in model solvent system. e.g. Triethylphosphate with or without salts (and/or proprietary solutions).
E	Emulsion aliquots from direct sampling of the product of emulsion polymerization employed for acceptance and blending decisions on each batch.
S	Solid dry powder polymer formed after processing and drying operations of the emulsion product.
R	Polymer solution in the solvent mixture of alcohols/amine and the mixtures of the model alcohols/amines such as cyclohexanol/isobutylamine.

Table 2. VEPA Performance Criteria, Sample forms, and Candidate Tests for QA/QC Specifications.

Performance	Sample Form	Intrinsic Test	Material Test
Viscoelasticity	Model Liquid and/or Proprietary Liquid (P)	FNSD ^a @125°C, Transient NF ^b Elongational	FNSD @25°C AppVis ^c Dynamic
	Solid (S)		Composition MW ^d
Homogeneity	Emulsion (E)		Particle Size MW MWD ^e
Processing/ Dissolution	Solvent Mix (R)	Time Dependent Viscosity LVN ^f LS ^g (MW, Rg ^h , and A2 ⁱ)	
Stability	Solvent Mix (R)	Time Dependent Viscosity LVN LS (MW, Rg, A2)	

- a. First Normal Stress difference.
- b. Normal Force.
- c. Apparent Viscosity.
- d. Molecular Weight.
- e. Molecular Weight Distribution.
- f. Limiting Viscosity Number.
- g. Light Scattering.
- h. Radius of Gyration.
- i. Second Virial Coefficient.

2.4 Batch Size and Schedule

The goal based on technical considerations is to have the fewest batch numbers over a short time period and with the largest batch size. Blending of polymerized batches in the emulsion form to obtain a single, homogeneous batch is a possible processing step if a single polymerization cannot yield the full production inventory. Production considerations may require deviations from the technical goal.

2.5 Processing Conditions Required Based on Properties of Polymer and Polymer Solution

There are several specifications imposed upon the material evaluation techniques by the processing conditions, such as accurate emulsion sample preparation. Likewise, there are conditions imposed by the material upon the processing:

- 1) mechanical stress from mixing, pumping, spraying, etc. should not degrade the shear sensitive, high MW tail;
- 2) the processing equipment should not allow the sorption of moisture by the hygroscopic polymer solution or polymer itself; and
- 3) the processing equipment should be continuously sealed to avoid evaporative loss of volatile solvents that would concentrate the solution.

The methods developed to monitor the control and acceptance of the polymer and solution can be applied to evaluate the performance of the processing facilities in meeting the above criteria.

2.6 Documentation Requirements

A hierarchy of candidate specifications will be constructed ranging from rigorous, complex methods (for example, LS) to simple tests (for example, viscosity). The simplest set of adequate tests will be selected for specifications, with optional back-up by more sophisticated tests, for use as failure confirmation tests or troubleshooting.

Final characterization procedures/specification will be drafted in mil-spec format. One or more supporting R & D technical reports will be required. Interim reports should be modular components of the final report(s). Both an unclassified document and, if needed, a classified or for-official-use-only appendix will be drafted.

3. CANDIDATE METHODS

3.1 Overview

To produce the desired properties in the end-use, the MW and MWD of VEPA must be within a certain range. Additionally, certain properties of the thickened solution must be determined to assure that it is a thermodynamically good solution which will remain stable during long periods of storage.

Currently, no standard test methods are available for acceptance/rejection of either VEPA or VEPA solution. Candidate test methods for specification of VEPA are the following characteristics;

1. concentration of the VEPA in the solution,
2. viscosity and viscoelasticity of the VEPA solution (MTL/CRDEC),
3. thermodynamic parameters of the VEPA solution in the form of R or P (MTL),
4. composition (monomer ratio) of VEPA (CRDEC/MTL),
5. distribution sequence of the monomer units in the VEPA,
6. ranges of impurities such as residual monomers, residual emulsifiers, and moisture (CRDEC/MTL),
7. average MW including number average MW (\overline{M}_n), weight average MW (\overline{M}_w), z-average MW (\overline{M}_z), etc. (MTL),
8. MWD, absolute or relative fraction in high MW tail; i.e., fraction whose MW's larger than 10 megadalton (MTL), and
9. solubility and gel fraction of VEPA in end-use solvent and/or test solvents (MTL).

Since VEPA is a high MW copolymer and the thickened solution consists of VEPA dissolved in a volatile, multi-component air/moisture sensitive solvent system, the analysis and testing of these can be quite complex. Furthermore, currently available standard test methods (such as ASTM) for MW and MWD of the polymers are not applicable for the complex copolymers and there are no test methods which directly assess some of the thermodynamic properties of the thickened solutions. Also, there is a need to refine/develop the methods to characterize solubility of the VEPA or viscosity/viscoelasticity of the thickened solution. A brief outline of such methods either in development or refinement for a similar polymeric additive is shown in Appendix A.

Generally accepted methods for characterization of polymer systems are summarized in Table 3. The rows list methods currently employed in general polymer chemistry which can be developed and applied to the copolymer system. The first column shows a preliminary estimate of the level of skill required as an operator/analyst for each method. 'High' infers that an operator is required to have a post graduate degree (MS and/or PhD) or equivalent experience. 'Medium' means the level of a chemist's degree (BS) or equivalent experience is required and 'Low' means no prior experience/training is required. However, training in the particular method would be required. The second column represents expense of the method, i.e., the cost of installation of the equipment as well as the cost for each analysis. The third column shows the predicted/projected application. Site was determined by the factors such as how troublesome a method is to be installed and maintained, how much skill an operator needs, and how much each method costs, etc. The properties one can deduce from each analysis are listed in the next sub-column, and the projected effectiveness of each analysis in the next.

3.2 Candidate Characterization Methods

3.2.1 Concentration of the VEPA.

Concentration of the VEPA in the solution can be determined by several conventional techniques. Examples of these techniques are gravimetric methods, refractive index measurement, and various spectroscopic methods.

3.2.2 Viscosity and Viscoelasticity of the VEPA Solution.

(1) Viscosity : Additional viscosity methods (different from the dilute solution viscosity (DSV) technique) may be used to characterize the concentrated solution. The current methods used to measure the concentrated solution viscosities are not adequate for the following reason; an open system allows the evaporation of volatile solvent components which will change the solvent composition, thus the solution viscosity changes with time. An appropriate viscosity technique would be a closed system that determines absolute viscosities. Several viscometers of the capillary, falling ball or falling needle type meet these criteria, and could be utilized for determining accurate concentrated solution viscosities. The magnetic needle rheometer (MNR), currently under development in the laboratory of Professor Ben Chu at the State University of New York at Stony Brook, will be developed and utilized for this purpose. A brief description of MNR is given in Appendix B. This MNR should have all the advantages of falling ball or falling needle type viscometers plus the ability to measure additional rheological properties.

Table 3. Evaluation of the Polymer Characterization Methods which can be employed for the QA/QC of the Thickener and/or Thickened Solution.

Characterization Method	Required Skill Level ^a	Estimated Cost		Predicted Application		
		Instr ^b	per Run ^c	Site ^d	Prop ^e	Eff ^f
Solubility Test	L	L	L	D	I,C	M
Gel Fraction	L-M	L	L	D	C,M	M
<u>Viscosity</u>						
Capillary	L	L	M	D	I,M	M
FNV ^g	M	L-M	L	D,R	I,M	M-H
Brookfield	M	L-M	L	D	M	M
MNR ^h	H	H(?)	L	R	I,M	M-H
LVN	M	L	H	R	M	H
SEC	H	H	H	R	M	H
NMR	H	H	M	R	C	H
FTIR	H	H	M	R	C	H
Light Scattering	H	H	H	R	I,M	H
<u>Thermal Analysis</u>						
DSC	H	M	M	D,R	C	H
TGA	H	M	M	R	C	M
Rheology	H	H	H	R	I,M	H

- a. skill level: L-low, M-medium, H-high.
b. estimated cost of the instrumentation: L-less than 10K, M-10K to 20K, H-more than 20K.
c. estimated cost per sample(measurement): L-low(less than 3 man-hrs), M-medium(4 to 8 man-hrs), H-high(more than 9 man-hrs).
d. probable analysis site: D-army depot, R-research laboratory.
e. property relationship which can be obtained: I-interaction of polymer with solvent/other, M-molecular weight, C-composition.
f. predicted effectiveness when the method is fully understood: L-low, M-medium, H-high.
g. Falling Needle Viscometer.
h. Magnetic Needle Rheometer.

(2) Viscoelasticity : In an attempt to obtain the relationship between viscoelasticity of the solution and end-use performance, experiments were carried out at CRDEC. However, the data obtained were scattered. It is desirable, therefore, to carry out a series of experiments to determine a more precise relationship. From this relationship, the acceptable range of the viscoelasticity of the solution can be obtained. The test method currently employed by CRDEC utilizing Rheometrics Fluid Rheometer model RFR 7800 can be employed with little modification, once the acceptance criteria are established.

3.2.3 Thermodynamic Parameters of the Thickened Solution.

The long term stability of the VEPA solution can be monitored using the technique of dynamic light scattering (DLS). An apparent self diffusion coefficient can be determined from DLS measurements, and this diffusion coefficient should not change with time, if the solution remains thermodynamically stable. DLS of the concentrated solution is desirable since the thickened solution can be monitored directly from the storage containers without a sample preparation step. Additionally, no impurities will be introduced by diluting the sample, and no assumptions have to be made in correlating the dilute solution properties with the concentrated rheological behavior.

3.2.4 Composition of the VEPA.

Both ^{13}C and ^1H NMR spectroscopy developed by CRDEC researchers will be refined and compositional specifications will be established. Other standard methods widely employed for polymer characterization in general, such as elemental analysis (EAN) and titration, might be refined and established as standard tests for the copolymer composition. Also, FTIR and thermal analyses (DSC and TGA) might be developed into characterization methods for the VEPA composition. Monomer composition as a function of MW (compositional drift) will be determined by fractionation with preparative size exclusion chromatography (SEC) followed by appropriate characterization(s).

3.2.5 Distribution Sequence of the Monomer Units in the Copolymer.

Determining the distribution sequence of the monomer units in a copolymer is a very complex problem. It is especially difficult in this study since the chemical structure of the comonomers are similar. A general approach for this problem is to utilize the corresponding low MW analogues (model oligomers). Examples of the methods used in this kind of research are spectroscopic methods such as NMR and FTIR.

Also applicable is the measurement of glass-transition temperature (T_g) by DSC or thermomechanical analysis (TMA). In general, T_g of a copolymer depends not only on the composition but also the distribution of monomer units. In other words, a random copolymer would show one T_g while a block copolymer would show two or more T_g 's in between the T_g 's of the corresponding homopolymers.

3.2.6 Impurities.

Impurities such as residual monomers, residual emulsifiers, and moisture can effect the end-use performance significantly. Thus, it is of importance to establish the relationship between the impurity contents and performance of the system. Utilizing the relationship, the characterization method(s) and acceptance criteria of the impurity contents will be developed.

Acceptance criteria of residual monomer(s) and residual emulsifier contents will be established by refining/developing/employing appropriate methods such as ^1H and ^{13}C NMR, FTIR, MSR, gravimetric methods, etc.

Acceptable range of the moisture content in the copolymer as well as the copolymer solution will be specified and determined by well-established methods such as Karl-Fischer and/or similar methods.

3.2.7 MW and MWD of the Copolymer.

The most important indirect or secondary material property test concerns quantification of the high MWD tail. Viscoelastic properties of solution correlate to the 8th power of MW^1 , therefore, most of the performance could be derived from the few percent of the higher MW portion of the sample. The majority of the polymer sample then serves only as a diluent. This range from critical high-performance, high MW tail to average MW diluent is a continuum. Viscoelastic measurements by Vinogradov (USSR) on fractionated polymer have shown the lower MW components of the MWD have a negligible influence.

The relevant specification is (1) the absolute concentration (g/dL) of high MW polymer portion and (2) what is actually dissolved and in the solution. Measurement of absolute concentration of MW larger than 7 megadalton, for example, is a non-routine specification. The more routine relative measurement of average MW statistics can be employed if (1) the polymerization process yields reproducible MWD especially with respect to ratio of high MW fraction to MW averages, (2) an SEC method can

1. Vinogradov, G.V. and Malkin, A. Ya., Karl Weissenberg 80th Birthday Celebration Essays, pp 65-79, John Harris Ed., 1973.

be developed to reproducibly quantify the MWD, and (3) the high MW fraction dissolves in the solvent mix in proportion to its overall distribution.

DSV, laser light scattering (LS), and aqueous and/or non-aqueous SEC test methods will be developed to analyze the average MW's (i.e., \overline{M}_n , \overline{M}_w , \overline{M}_z , \overline{M}_{z+1} , etc.) of the copolymer. Currently, standard test methods exist for the techniques of DSV, LS, and non-aqueous SEC; however, the specific problems associated with copolymer characterization are not addressed in these test methods.

(1) DSV : Based on the standard method (ASTM D446-85a), DSV will be developed and specifications for the copolymer will be established for the limiting viscosity number (LVN) along with Huggins and Kraemer constants. Also specified will be at least 3 different solvents other than the multi-component solvent system currently employed.

(2) LS : Test methods based on LS currently employed by MTL researchers (G. Hagnauer and M. Potts) will be developed to characterize the size of the polymer in terms of MW and radius of gyration (Rg). The acceptance criteria of these properties will be established as well as the solvent system(s) to be used in this test method.

(3) SEC : The aqueous SEC method employed by the Rohm and Haas company with similar polymer systems will be refined for the copolymer system. Alternately, the non-aqueous SEC method will be developed from the standard SEC methods. The ranges of the different MWs (i.e., \overline{M}_n , \overline{M}_w , \overline{M}_z , \overline{M}_{z+1} , etc.) will be specified and the algorithm to be used in calculation of these values will be specified or developed.

(4) Other : Since the high MW portion of a VEPA would have a larger influence on viscoelasticity of the solution, methods such as ultracentrifugation and Sedimentation Field Flow Fractionation (SFFF) might be studied and established as test methods. However, these methods are very costly to install/maintain and require extensive study for the utilization in this program. Thus, these are not high priority candidates. Also applicable in this category are different fractionation techniques. For example, certain membranes (of specified pore size) can separate the fraction of polymer with high MW from the fraction of lower MW.

3.2.8 Solubility and Gel-Fraction.

(1) Solubility : The standard solubility test method (ASTM D3132-84) will be developed into a preliminary test for an acceptance criterion. The list of the solvents to be used and their priorities are currently under consideration (examples of these are shown in Table 4).

(2) Gel-Fraction : A gravimetric method related to the ASTM method (D2765-84) can be developed and employed. For example, the copolymer sample could be placed in a to-be-specified solvent(s), followed by centrifugation, decantation of the liquid phase, and drying. The dried fraction then can be weighed for gel-fraction. Alternately, microfiltration (with pore size to be specified) can be employed in place of centrifugation. Also specified will be the acceptance criteria of the gel-fraction.

4. SUMMARY

Based on an evaluation of the material properties that control fluid dynamic performance, a number of conclusions, recommendations and technical plans can be advanced. For the QA/QC surveillance of a VEPA, a variety of material property test methods will be studied. The results of these tests then will be correlated to the performance criteria of the VEPA. According to these correlations, a hierarchy of test methods will be constructed and the simplest set of adequate tests will be selected for the QA/QC surveillance. Also, more rigorous, complex methods which can be served as back-up test methods will be selected. Numerical ranges of the specification will be determined for each test method selected.

GLOSSARY

A ₂	Second Virial Coefficient
ASTM	American Society of Testing Materials
¹³ C	Carbon 13
DLS	Dynamic Light Scattering
DSC	Differential Scanning Calorimetry
DSV	Dilute Solution Viscometry
EAn	Elemental Analysis
FNSD	First Normal Stress Difference
FTIR	Fourier Transformation Infrared Spectrophotometry
¹ H	Proton
LS	Light Scattering
LVN	Limiting Viscosity Number
<u>M_n</u>	Number Average Molecular Weight
<u>M_w</u>	Weight Average Molecular Weight
<u>M_z</u>	Z-average Molecular Weight
<u>M_{z+1}</u>	Z+1-average Molecular Weight
MW	Molecular Weight
MWD	Molecular Weight Distribution
MSR	Magnetic Sphere Rheometer
NMR	Nuclear Magnetic Resonance
R _g	Radius of Gyration
SEC	Size Exclusion Chromatograph
SFFF	Sedimentation Field Flow Fractionation
TGA	Thermal Gravimetric Analysis
VEPA	Viscoelastic Polymer Additive

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APPENDIX A
SPECIFICATION TEST METHODS
AND ACCEPTANCE CRITERIA
FOR 100LB METHACRYLATE COPOLYMER

All the tests listed below will be conducted at an independent laboratory not affiliated with the bidder. CRDEC reserves rights to confirm the results at another independent laboratory. Either CRDEC or the bidder can conduct the test(s) upon mutual agreement. CRDEC also reserves the right to improve/change any of the below listed procedures and the resulting acceptance criteria.

CRDEC has a reference copolymer (lot CM1-120) for comparison of test results under identical conditions. Comparative testing of the reference vs procured sample will be blind and randomized. The reference vs procured sample will have equivalent variances at $\alpha=0.05$. Sample size will be 3 or larger.

Specifications

1. Molecular weight of 3 million or higher estimated from viscosity data and/or size exclusion chromatography (SEC).

1a. Dilute solution viscosity will be conducted using a capillary viscometer according to ASTM D446-85a. The limiting viscosity number(LVN) along with Huggins and Kramer constants will be determined in at least 3 different solvents. The solvents include, but are not limited to, 2-methylcyclohexanol, N-methyl-2-pyrrolidone, and isopropylamine. All the resulting LVN's will be larger than those of the reference copolymer lot CM1-120 obtained under the identical condition, with variances that are not statistically different.

1b. Aqueous SEC method will be employed. A brief summary of the methodology is enclosed as Appendix A. Alternately, the nonaqueous SEC method under development at MTL can be applied. The resulting weight average molecular weight (\overline{M}_w) of the copolymer should be equal to or higher than 3.0 million (3.0 megadaltons). \overline{M}_w will be calculated from distribution by standardized commercial algorithm. The molecular weight distribution (MWD), i.e., the ratio of \overline{M}_w versus number average molecular weight (\overline{M}_n) will be smaller than 5.

2. Composition of the copolymer to be;
 - * 20 to 25 mole % t-butylaminoethyl methacrylate.
 - * 75 to 80 mole % isobutyl methacrylate.By NMR spectroscopy and/or similar methods.

Both ^{13}C and ^1H NMR of the copolymer in deuterated chloroform (CDCl_3) will show the tBAEMA content between 20 to 25 mole %. Alternately, elemental analysis and/or titration can be employed for the determination of the copolymer composition.

3. Dried (under vacuum at lower than $40^\circ\text{C}.$);
 - <1 % moisture content.

Moisture content will be determined by well established Karl-Fischer and/or similar method and should be lower than 1.0 % wt/wt.

4. Residual monomer content; <1 wt.%.

Residual monomer content will be determined by both ^{13}C and ^1H NMR methodology developed at CRDEC and should be less than 1.0 % wt/wt.

5. No crosslinking by gel fraction determination;
 - method to be specified by CRDEC.

A gravimetric method can be employed. For example, put the copolymer in a given proprietary solvent (or, a solvent mixture to be specified and/or supplied by CRDEC), centrifuge, decant the liquid phase, dry and weigh the gel fraction. Alternately, micro filtering ($0.45\ \mu$ or smaller pore size) can be used in place of centrifugation. The gel fraction thus determined will be less than 1.0 % wt/wt.

6. Random distribution of monomer units by gradual addition of monomers during emulsion polymerization.

The gradual addition of monomers during the emulsion polymerization will be achieved by continuous pumping, not by incremental addition. Determination of random distribution of monomer units by NMR spectroscopy can also be employed.

7. Monomodal molecular weight distribution by SEC, without apparent shoulders relative to reference SEC of copolymer Lot CM1-120 (will be provided by CRDEC).

Chromatogram of the procured copolymer will be compared to the reference copolymer lot CM1-120 chromatograms. Reference copolymer and/or the SEC condition will be provided by CRDEC.

8. Solubility up to 10 g/dL in the nonaqueous, multi-component organic solvent (the solvent to be provided by CRDEC or the solubility to be tested at CRDEC).

Solubility test will be conducted according to the ASTM D3132-72, and the copolymer should be completely soluble in the multi-component organic solvent.

9. Including a specification sheet on molecular weight analysis, viscosity data, SEC analysis data, composition data, solubility test data (including LVN data), process recipe, and sensitivity to process parameters.

NOTE : Government will provide process recipe previously used for 12 lb batch size with molecular weights of 2-3 megadaltons.

The recipe for 12 lb lab scale emulsion polymerization will be provided.

10. The entire quantity must be produced in one batch, 100 lb or greater, not a blend of smaller lots.

CRDEC will optionally send personnel to confirm the one batch process.

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APPENDIX B

A BRIEF DESCRIPTION OF MAGNETIC NEEDLE RHEOMETER

The Magnetic Needle Rheometer (MNR)¹, is a microprocessor-controlled device capable of measuring viscosities in the range of 50 cP to 5×10^7 cP and viscoelastic relaxation times from 0.1 second to 1 hour. The shear rate can be varied from 1 to 2×10^{-4} per second. In addition, the sample can be hermetically sealed with an inert (glass enclosed) magnetic probe to allow the analysis of hazardous or volatile materials.

The principle of operation of the MNR is as follows: A small (ca. 1 mm x 5 mm) magnetic stir bar is sealed inside a glass capillary tube and placed inside a glass vial (sample cell) with the sample to be analyzed. The sample cell is placed inside a cylindrically-shaped wire coil. A current flowing through the coil creates a magnetic field which levitates and maintains the needle at a given height. A laser is positioned such that it illuminates the area of the needle and casts a shadow of the needle on a detector. This position-sensitive detector determines how far the shadow of the needle is from a predetermined "null" position. This information is fed to a computer which then calculates the amount of current required to bring the position of the needle back to its "null" position. The computer then sends this information to a current generator which supplies the required current to the coil. The amount of current fed to the coil is read by a current meter, and sent back to the computer to be recorded in a data file. This feedback mechanism between the detector, the computer, the current generator, and the current meter occurs about 400 times/second to keep the needle stable at a given height.

Concurrently, a motor moves the cell vertically to create viscous drag of the liquid against the stationary needle. The motor used to control the movement of the cell is driven in mini-steps, and therefore can be used at speeds as low as 0.1 microns/second, and thus very low shear rates can be obtained. As this viscous force is created, the current required to keep the needle levitated increases, and this increase in current (relative to the amount of current required to levitate the needle when the cell is stationary) is proportional to the coefficient of viscosity of the liquid. Liquids of known viscosity are used to determine the proportionality constant between the current increase and the viscosity.

1. Rev. Sci. Instrum. 60(4), 760, April 1989.

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SUPPLEMENTARY

INFORMATION

DEPARTMENT OF THE ARMY
U.S. Army Chemical Research, Development and Engineering Center
Aberdeen Proving Ground, Maryland 21010-5423

ERRATUM SHEET

24 May 1991

Report No.: CRDEC-TN-012

Title: Specification Development for a Viscoelastic Polymer
Additive Based on Correlations Between Performance
Criteria and Material Characterization Tests


Author: Wendel J. Shuely
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Research Directorate

Marie K. Potts
U.S. Army Materials Technology Laboratory

Date: December 1989

Report
Classification: UNCLASSIFIED

Replace pages 3 and 4 with the attached pages.

for 
Joseph J. Vervier
Director, Research Directorate

AD-A218205

PREFACE

Technical notes are published by the U.S. Army Chemical Research, Development and Engineering Center (CRDEC) as a quick method to disseminate information to a limited audience. This information may be superseded or appear later in a CRDEC technical report or special publication.

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This report has not been approved for release to the public.

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