ACUMER™ 1000, ACUMER 1020 ACUMER 1100, ACUMER 1110 Scale Inhibitors

Description

These ACUMER™ polymers are a series of Low Molecular Weight (LMW) Polyacrylic Acids and their corresponding sodium salts. These products have weight average molecular weights of approximately 2000 and 4500. ACUMER polymers contain no phosphorus, making their use acceptable where legislation requires that discharge waters contain low or no phosphorus.

ACUMER polymers are highly effective scale inhibitors that can be used industrial water treatment and oil production applications to inhibit the deposition of calcium carbonate, calcium sulfate, barium sulfate, and other low solubility salts on surfaces. These polymers show good activity over a wide range of pH, water hardness, and temperature conditions. The choice among the members of the series depends on the application, formulation, use conditions, and required performance characteristics. These materials show excellent freeze-thaw stability.

Typical Properties

This ACUMER™ series consists of polymers as unneutralized, partially neutralized (20%) and fully neutralized forms as shown in Table 1. Molecular weights are measured by aqueous gel permeation chromatography (GPC). Representative data for ACUMER 1000/ACUMER 1020 polymers are depicted in Figure 1.

Figure 2a is a plot of the degree of neutralization vs. pH for the ACUMER polymers. Figures 2b-e show the effect of caustic additions to ACUMER 1000 and ACUMER 1100 on product pH.

Typical Physical Properties

Table 1

(These properties are typical but do not constitute specifications.)

Polymer	Form	Molecular Weight[1] $\bar{M}_w$	Molecular Weight[1] $\bar{M}_n$	Appearance	% Total Solids	Density 25°C lbs/gal	pH	Viscosity 25°C, cps	Spindle Speed
ACUMER 1000	Partial Na Salt 20% Neutralized[2]	2000	1425	Colorless to straw colored, clear to slightly hazy homogeneous solution.	48	10.3	3.6	200	#2 @ 30
ACUMER 1020	Acid	2000	1425		39-41	10.1	2.1-2.5	<1000	#1 @ 60
ACUMER 1100	Partial Na Salt 20% Neutralized[2]	4500	3000		48	10.2	3.6	800	#3 @ 60
ACUMER 1110	Na Salt	4500	3000	Colorless to straw colored, clear to slightly hazy homogeneous solution.	45	11.1	7.2	850	#2 @ 12

[1]Weight Average ($\bar{M}_w$) and Number Average ($\bar{M}_n$) Molecular Weight expressed as polyacrylic acid (PAA).

2Requires 0.30-0.35 lbs NaOH/lb product solids for 95% neutralization.

FIGURE 1 — MOLECULAR WEIGHT DISTRIBUTION FOR ACUMER 1000/ACUMER 1020 BY AQUEOUS GPC

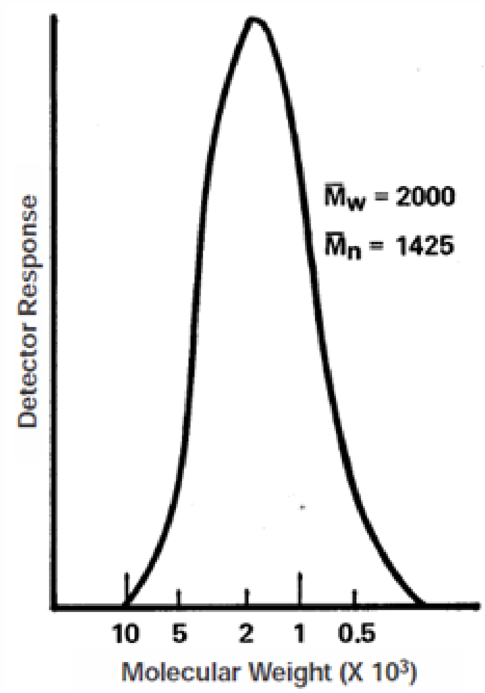


FIGURE 2a — NEUTRALIZATION OF ACUMER POLYMERS

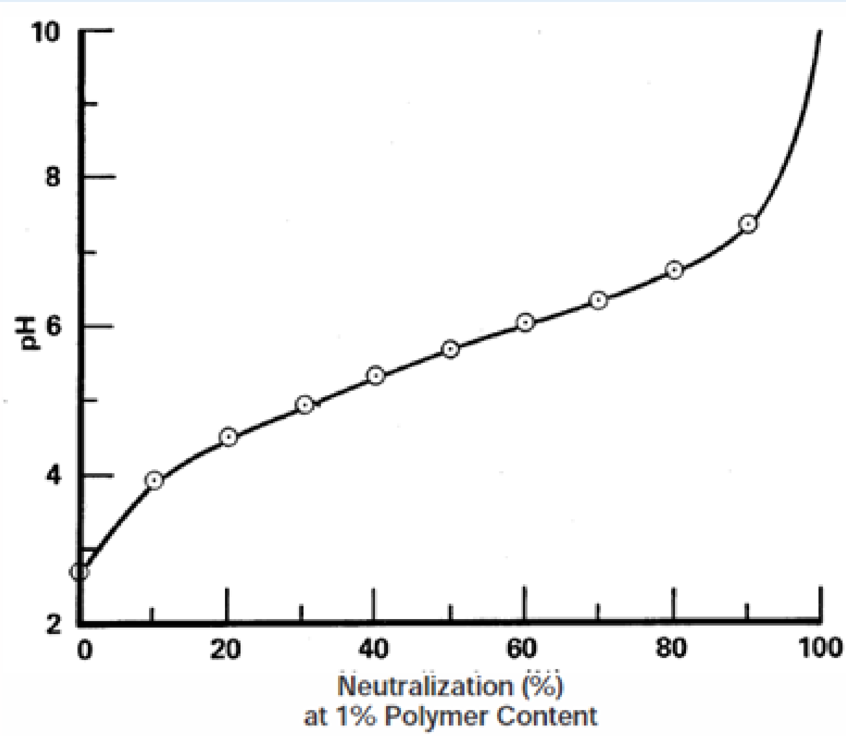


FIGURE 2b — NEUTRALIZATION OF ACUMER 1000/ACUMER 1100 (PRODUCT) WITH KOH (45%)

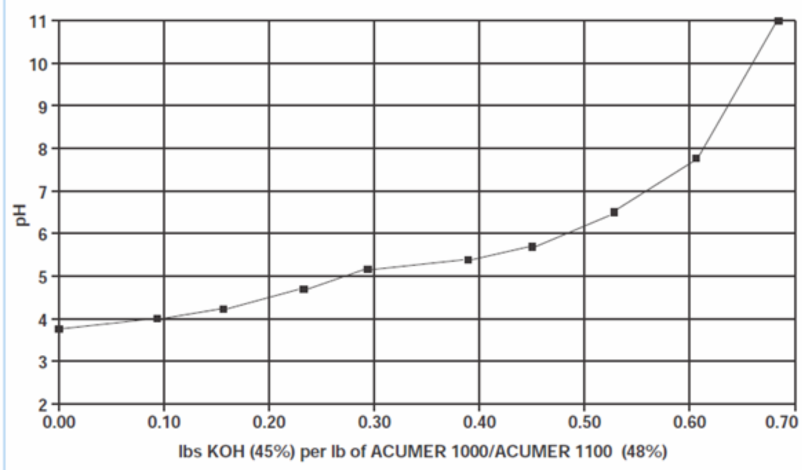


FIGURE 2c — NEUTRALIZATION OF ACUMER 1000/ACUMER 1100 (PRODUCT) WITH NaOH (50%)

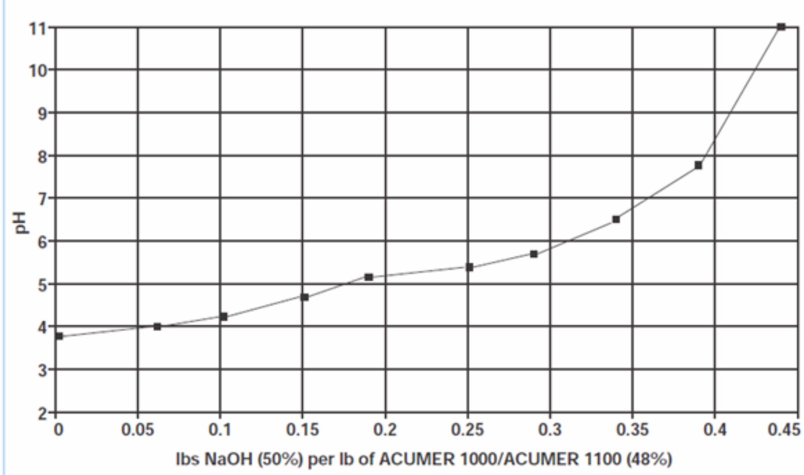


FIGURE 2d — NEUTRALIZATION OF ACUMER 1000/ACUMER 1100 (SOLIDS) WITH KOH (45%)

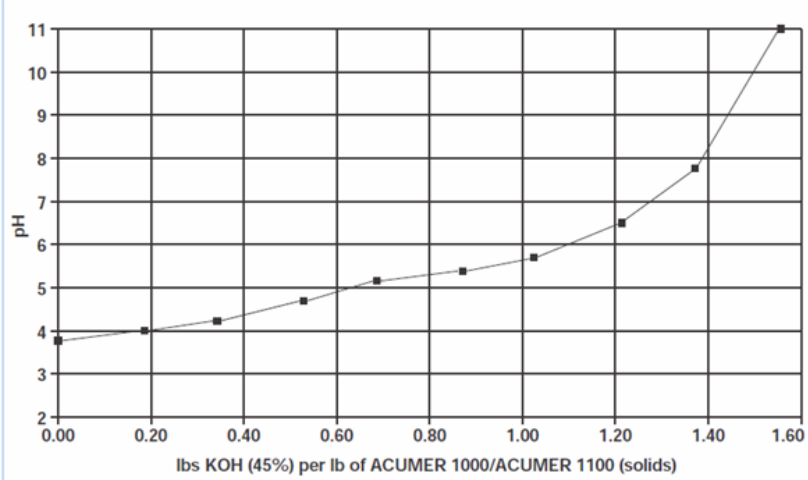
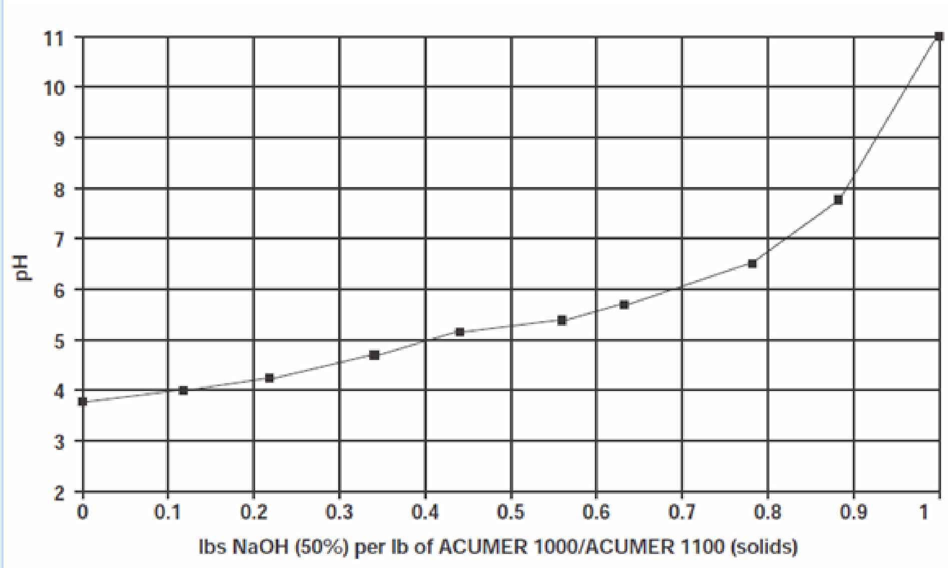


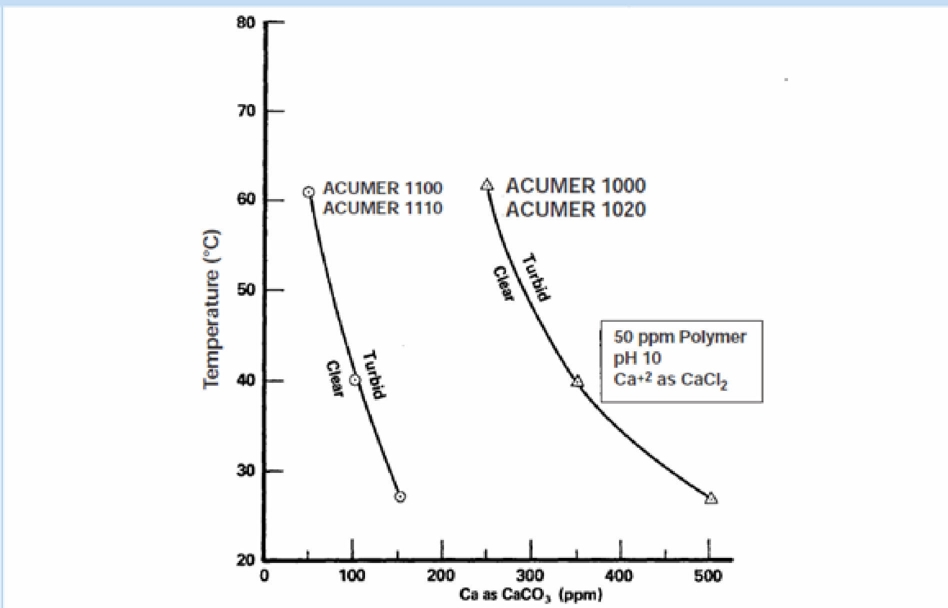
FIGURE 2e — NEUTRALIZATION OF ACUMER 1000/ACUMER 1100 (SOLIDS) WITH NaOH (50%)



Solubility

The effects of Ca^{+2} concentration and temperature on the solubility of the ACUMER™ polymers are illustrated in Figure 3. Increasing Ca^{+2} concentration and temperature can lead eventually to some degree of insolubility. The solubility of these polymers tends to decrease with increasing calcium levels and temperature. ACUMER 1000 and ACUMER 1020 are more soluble than the higher molecular weight polymers, ACUMER 1100 and ACUMER 1110. All of the ACUMER polymers, however, show some solubility and provide activity at points above the curves, since these are merely the start of insolubility, and much of the polymer remains soluble in the temperature/concentration regions above those represented by the areas above the curves.

FIGURE 3 — POLYMER SOLUBILITY AS A FUNCTION OF HARDNESS AND TEMPERATURE



ACUMER™ polymers also exhibit good solubility in brine solutions. The following Table 2 showing percent transmittance as a function of salinity indicates that the solubility of a given polymer actually increases with increasing salinity. In experiments generally, clarity of the solution measured as percent transmittance is used as an indicator of solubility.

Table 2
Solubilities as a Function of Salinity

Polymer	0% NaCl	% Transmittance at 60°C 500 ppm NaCl	50,000 ppm NaCl
ACUMER 1000/ ACUMER 1020	46	51	82
ACUMER 1100/ ACUMER 1110	Insoluble	30	60
All solutions contain 100 ppm polymer solids and 3000 ppm Ca^{+2} as $CaCO_3$ (1200 mg/l Ca^{+2}).			

Stability in Hypochlorite Solutions

ACUMER™ polymers exhibit exceptional stability in the presence of hypochlorite as compared with other commercially available polyacrylic acids (Table 3).

Table 3
Stability of Polyacrylic Acids in Hypochlorite Solutions[a]

Polymer	14 days	Loss of Chlorine, % After days at 40°C 21 days	42 days
None	4.3	10.3	20.2
ACUMER™ 1100/ACUMER 1110	7.1	11.1	18.6
ACUMER 1000/ACUMER 1020	7.8	11.3	-
Polymer G	21.5	26.9	34.1
Polymer AC	19.5	26.8	-
Polymer C	42.3	54.1	-
Polymer A	39.7	48.2	-
Polymer M	51.0	57.6	-

[a]Solutions contain 10% NaOH/2% polymer (solids)/2% NaOCl.

Applications

ACUMER™ polymers can be used to inhibit scale buildup on surfaces through at least three mechanisms:

- Solubility enhancement or threshold effect, which reduces precipitation of low solubility inorganic salts.
- Crystal modification, which deforms the growing inorganic salt crystal to give small, irregular, readily fractured crystals that do not adhere well to surfaces.
- Dispersing activity, which prevents precipitated crystals or other inorganic particulates from agglomerating and depositing on surfaces.

Low molecular weight polyacrylic acids are widely used to inhibit scaling in industrial water treatment and in oil production applications. The activity of the ACUMER polymers in cooling tower, boiler, and oil field applications is illustrated by the following data.

Scale Inhibition at Heat Transfer Surfaces

In evaluating scale inhibition at heat transfer surfaces, the ACUMER™ polymers were used alone under stressed conditions. Note that their relative effectiveness may change in formulated water treatment systems or under less stressed conditions.

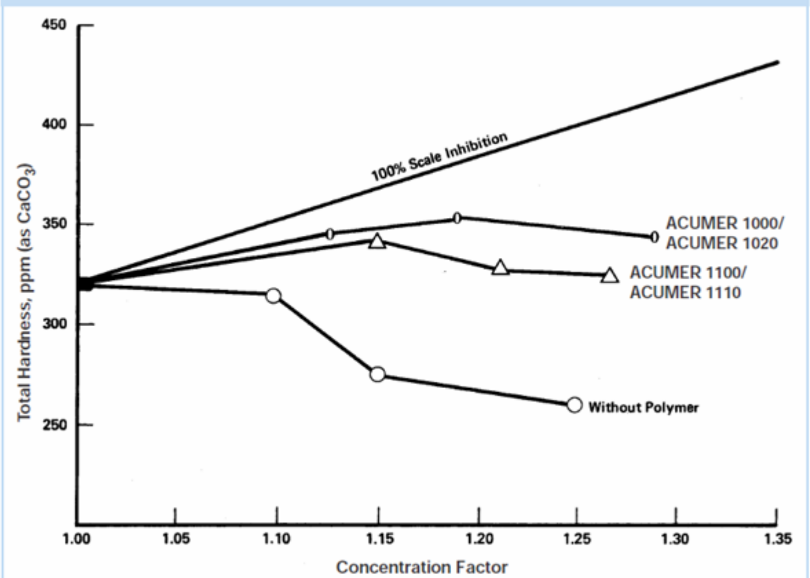
1. Laboratory Test on Immersion Heater (Table 4, Figures 4 and 5)

   Test water was recirculated past an immersion heater and over baffles exposed to upward air flow; Table 4 lists the test parameters. During the 3-hour run, the calcium ions remaining in solution as evaporation proceeded and the rate of heat transfer (time the heater was on) were monitored. The amount of scale deposited on the heater at the end of the test was also measured. ACUMER 1000/ACUMER 1020 ($\overline{M}_w$ 2000) were the most effective under these conditions by all three measurements of scaling tendency. The highest molecular weight analogs ACUMER 1100/ACUMER 1110 ($\overline{M}_w$ 4500) and a competitive sodium polyacrylate ($\overline{M}_w$ 2800) were less effective.

Table 4
Immersion Heater Test Parameters

Duration	3 hours
Temperature	60°C, maintained by immersion heater
Alkalinity	250 ppm (as CaCO3)
Total Hardness	320 ppm (as CaCO3), 9:1 Ca:Mg
Polymer Dosage	5 ppm solids basis
Water Volume (initial)	7.5 liters
pH (initial)	8.1
Air Flow	52.4 liters/minute
Water Flow	40 liters/hour
Langelier Saturation Index	+1.88
Ryznar Index	4.34 (heavy scaling tendency)

FIGURE 4 — IMMERSION HEATER TEST PERFORMANCE
TOTAL HARDNESS VS. CONCENTRATION FACTOR



Scale Inhibition at Heat Transfer Surfaces (Con't.)

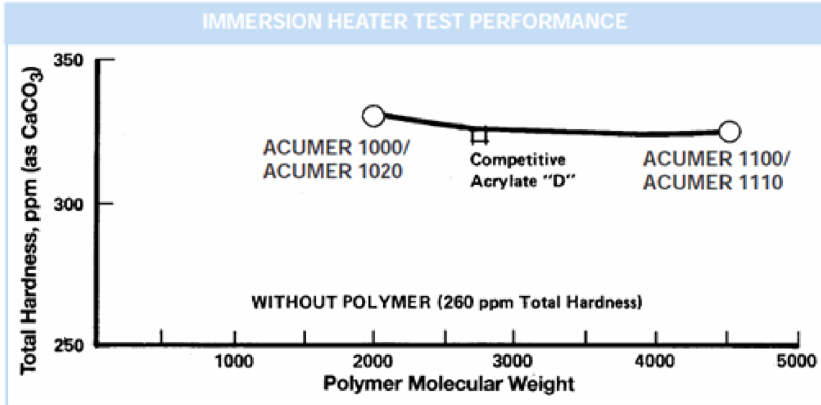


FIGURE 5A—ANTI-PRECIPITATION ACTIVITY

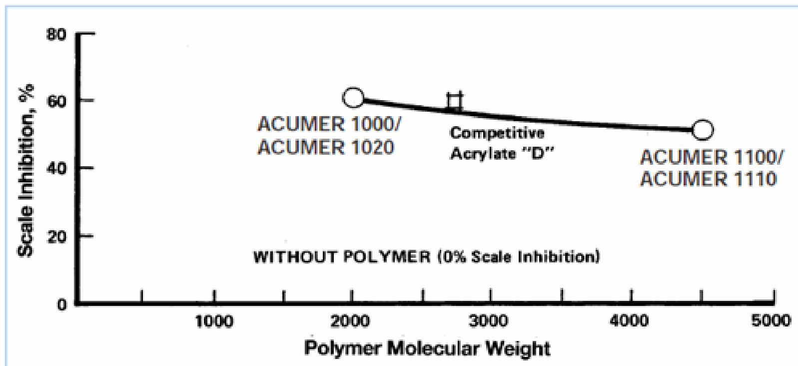


FIGURE 5B—SCALE INHIBITION

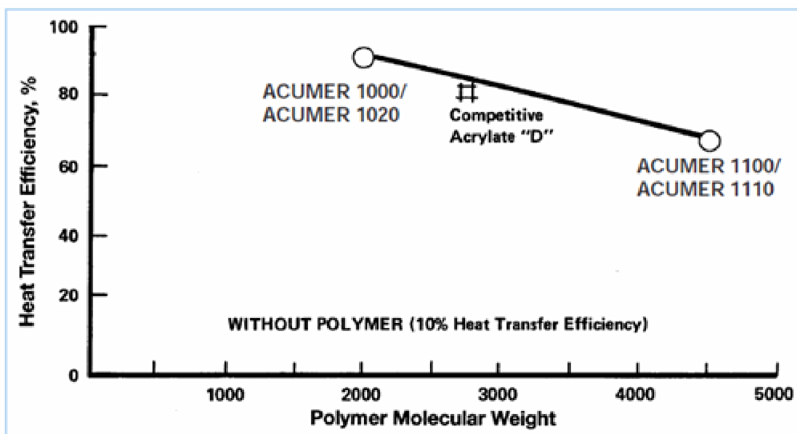


FIGURE 5C—HEAT TRANSFER EFFICIENCY

2. Simulated Cooling Tower Test (Tables 5 and 6)

   The relative performance of the ACUMER™ polymers was evaluated in simulated cooling tower devices under stressed conditions. Water containing 625 mg/l hardness (as $CaCO_3$) and 150 mg/l alkalinity was circulated past a copper heat transfer coupon at 0.4 to 2 ft./sec. in an apparatus designed to give a range of flow rates over a single heat transfer surface; Table 5 lists the test parameters. Heat transfer coefficients were monitored daily for 5 days; the polymer levels were 2.5, 7.5, and 15 ppm. Table 6 lists the average retained heat transfer coefficient at each polymer concentration. Like the immersion heater study, ACUMER 1000/ACUMER 1020 were the most effective polymers in maintaining a constant, high heat transfer coefficient and ACUMER 1100/ACUMER 1110 were almost as good.

Table 5
Simulated Cooling Tower Test Parameters

Duration	5 days
Total Hardness (as $CaCO_3$)	625 mg/l
Ca/Mg ratio	4/1
Na^+ content	250 mg/l
Alkalinity (as $CaCO_3$)	150 mg/l
pH	8.1-8.5
Heat flux	10,000-15,000 btu/hr./ft.[2]
Average water temperature	120°F (50°C)

Table 6
Retained Heat Transfer Coefficient, $\%u_c$[1]

Polymer	Initial	1 Day	5 Days
ACUMER 1000/ACUMER 1020	100	85.5	85.7
ACUMER 1100/ACUMER 1110	100	83.8	71.9

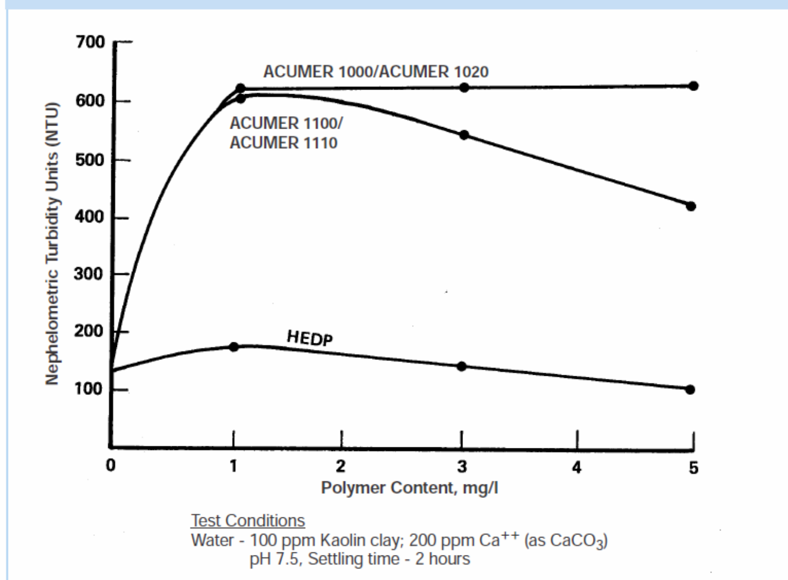
[1] $\%uc = (u_f / u_c) \times 100$
where u_f = fouled heat transfer coefficient
u_c = clean heat transfer coefficient

Dispersing Activity (Figure 6)

Industrial cooling water and many oil-field brines contain particulate matter such as silt, clays, and calcium-based precipitates. The particles can be deposited on heat transfer surfaces, produce excessive sediments in regions of low water velocity, and interfere with the flow of drive water through oil-field formations.

Kaolin clay was used to represent particles commonly found in many waters. At low polymer levels (<5 mg/l). ACUMER™ 1100/ACUMER 1110 and ACUMER 1000/ACUMER 1020 polymers are very effective. The ACUMER polymers are all better dispersants than the commercially used phosphonate (HEDP – 1-hydroxyethylidene-1,1-diphosphonic acid).

FIGURE 6 — DISPERSING ACTIVITY



Anti-Precipitation Activity

Most oil-field waters are brines, containing large amounts of divalent cations which commonly form mineral scales. Scale can be encountered on the formation face, in the production tubing, on surface vessels, injection pumps, lines, etc.

The scales of greatest concern in oil production are calcium sulfate, calcium carbonate, and barium sulfate. Laboratory screening tests are useful for comparing the effectiveness of inhibitor candidates. Details of the test procedures are given in the Appendix.

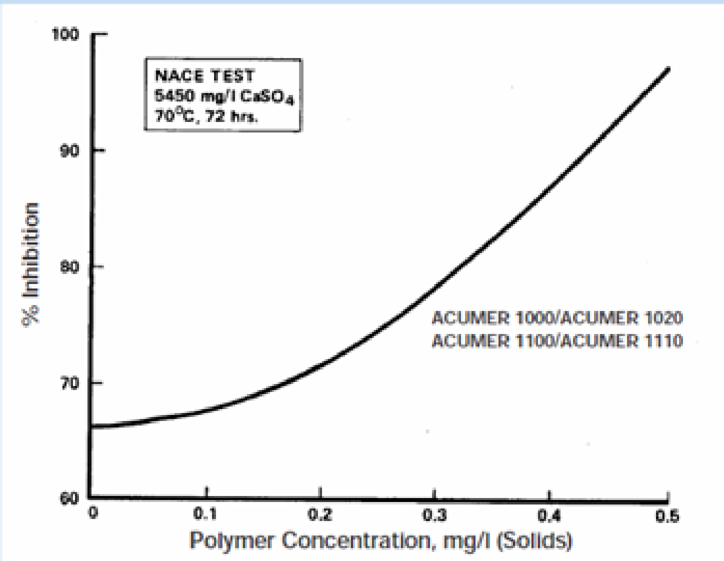
1. Inhibitor of $CaSO_4$ Precipitation (Figure 7)

   ACUMER™ polymers are all highly effective inhibitors of $CaSO_4$ precipitation. Virtually complete inhibition is achieved with 0.5 ppm polymer under the NACE test conditions. No significant difference in activity among the polymers in the ACUMER series is noted during this test.

2. Inhibition of $CaCO_3$ Precipitation (Figure 8)

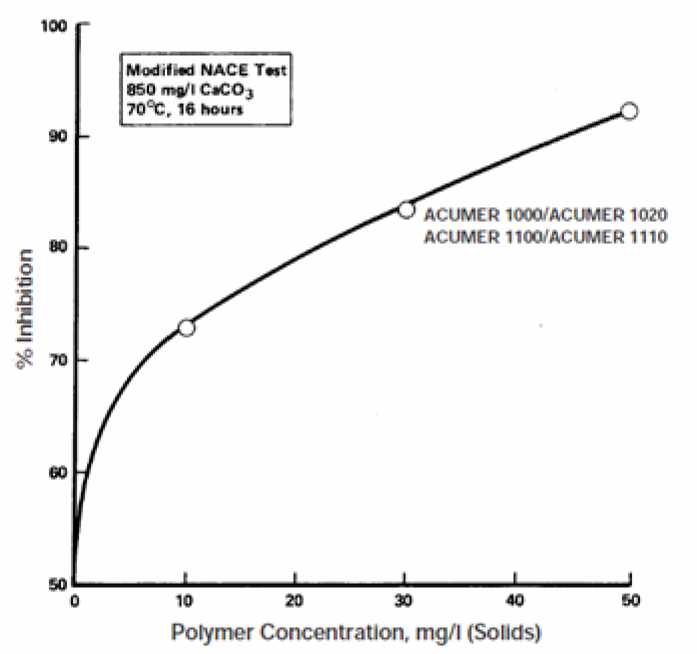
   ACUMER 1100/ACUMER 1110 ($\overline{M}_w$ 4500) and ACUMER 1000/ACUMER 1020 polymers ($\overline{M}_w$ 2000) are equally effective inhibitors of $CaCO_3$ precipitation.

FIGURE 7 — $CaSO_4$ ANTI-PRECIPITATION ACTIVITY



Anti-Precipitation Activity (Con't.)

FIGURE 8 — $CaCO_3$ ANTI-PRECIPITATION ACTIVITY



3. Inhibition by Blends of ACUMER™ Polymers and Phosphonates (Figure 9)

   In some instances, blends of phosphonates or phosphate esters with ACUMER polymers are better anti-precipitants than either alone. Figure 9 demonstrates the synergistic behavior of ACUMER 1100/ACUMER 1110 and phosphonate for calcium carbonate inhibition; the dotted lines plot the additive effects and the solid lines the actual effects of the blends.

4. Inhibition of $BaSO_4$ Precipitation (Figure 10)

   $BaSO_4$ scale is particularly difficult to remove and consequently prevention is critically important, especially in off-shore oil wells and papermaking applications. ACUMER 1000/ACUMER 1020 polymers ($\overline{M}_w$ 2000) are particularly effective in a typical 16-hour duration test and show more efficient inhibition than ACUMER 1100/ ACUMER 1110 ($\overline{M}_w$ 4500) polymers. ACUMER 1000/ACUMER 1020 polymers also show better inhibiting activity than a competitive sodium polyacrylate, a phosphonate, or a phosphate ester.

   If longer times (64 hours) are allowed for precipitation, ACUMER 1100/ACUMER 1110 ($\overline{M}_w$ 4500) are more effective than ACUMER 1000/ACUMER 1020 ($\overline{M}_w$ 2000).

5. Overall Anti-Precipitation Performance

   The actual choice between the two molecular weight polymers depends on the test conditions, although generally ACUMER 1000/ACUMER 1020 ($\overline{M}_w$ 2000) are the most effective polymers. At high Ca^{+2} concentration and high temperature, ACUMER 1000/ACUMER 1020 would be expected to perform better than ACUMER 1100/ ACUMER 1110 considering the comparative solubilities versus Ca^{+2} concentration and temperature in Figure 3.

Anti-Precipitation Activity (Con't)

MODIFICATION OF $CaSO_4$ AND $CaCO_3$ CRYSTALS (Figures 11 and 12)

The photomicrographs in Figures 11 and 12 show the dramatic crystal distortion effects of ACUMER 1000/ ACUMER 1020 and ACUMER 1100/ACUMER 1110 on $CaSO_4$ and $CaCO_3$. The normally long and regular $CaSO_4$ crystals are fractured and distorted when formed in the presence of ACUMER 1000/ACUMER 1020 polymers. $CaCO_3$ crystals are normally large and well formed, but are smaller and more irregular when formed in the presence of ACUMER 1100/ACUMER 1110.

Polymer Stability at High Temperature

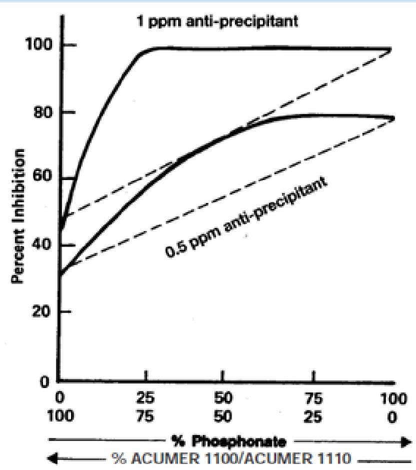
ACUMER™ polymers 1000, 1020, 1100 and 1110 are very stable at high pressures and temperatures typical of boilers up to at least 1200 psig/298°C. The chart below contains data on the hydrothermal stability of ACUMER 1000.

Hydrothermal Stability of ACUMER™ 1000 Polymer in Synthetic Boiler Water and Thermogravimetric Analysis (TGA) of the Solid Polymer as Sodium Salt

Temp/Press	Hydrothermal Stability[1]					TGA Analysis
	$\bar{M}_w$	$\bar{M}_n$	% M_n Loss	S.I.[2]	%COOH	Weight Loss
ACUMER 1000						
Initial	2090	1660	-	-	100	Stable
249°C/560 psig[3]	2010	1490	10.2	0.1	93	Stable
294°C/1142 psig	1850	1370	17.5	0.2	77	Stable
323°C/1686 psig	1180	717	56.8	1.3	58	Stable
340°C/>2000 psig	-	-	-	-	-	Onset of Degradation

[1]Test Conditions: 5000 ppm active ACUMER 1000/pH 11, purged with hydrazine, 24 hours.
[2]S.I. = scission index = no. of C-C bonds broken/molecule; (M_n initial/M_n after heating) $^{-1}$.
[3]1 psi = 0.689 kg/cm² (Bar).

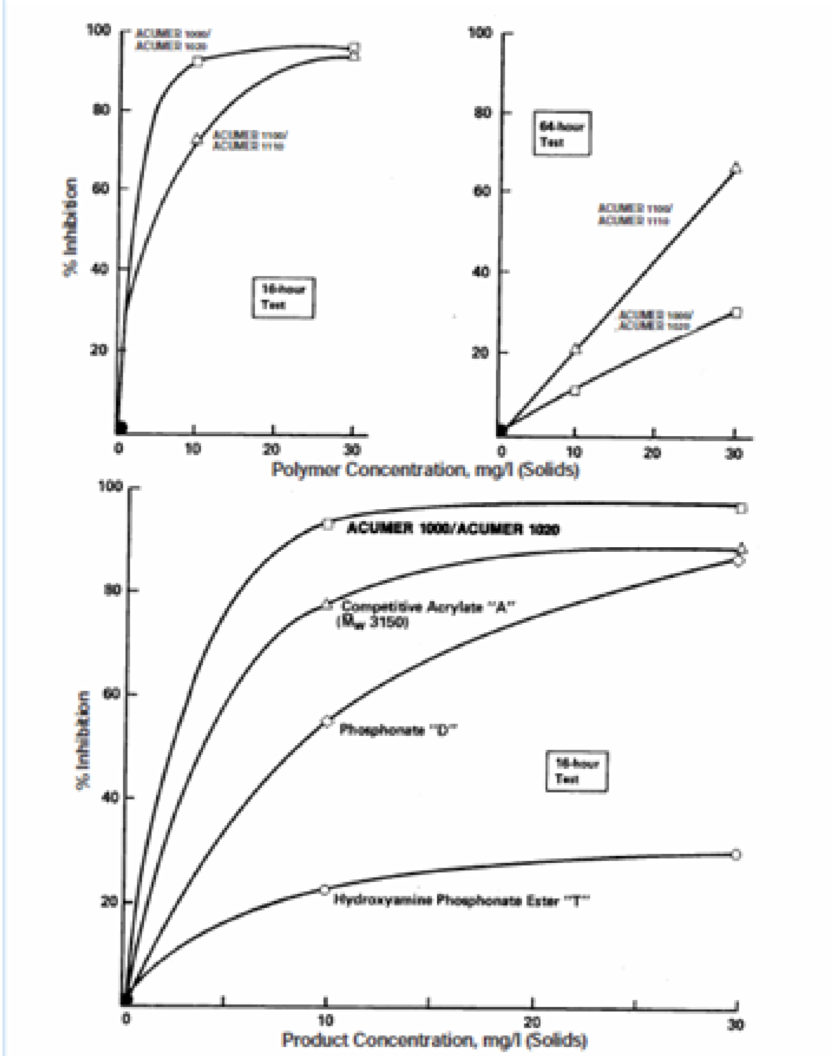
FIGURE 9 — CALCIUM CARBONATE ANTI-PRECIPITANT ACTIVITY OF BLENDS



Test Conditions
Water - 250 ppm $CaCO_3$; 30,000 ppm NaCl
Temperature - 85°C
Time - 24 hours

Polymer Stability at High Temperature (Con't)

FIGURE 10 — $BaSO_4$ ANTI-PRECIPITATION ACTIVITY (136 mg/l Ba^{+2}, 70°C)



Appendix

Anti-Precipitation Tests

1. $CaSO_4$ Test – NACE STANDARD TM-03-74

    1. Prepare supersaturated solution of 5450 mg/l $CaSO_4$ in brine containing 0-0.5 mg/l (solids) scale inhibitor.
    2. Store in capped 4-oz. jar in 70°C oven for 72 hours without agitation.
    3. Remove sample, draw off supernatant, test for Ca^{+2} using standard EDTA titration.

2. $CaSO_3$ Test (Modified NACE Test)

    1. Prepare supersaturated solution of 850 mg/l $CaCO_3$ in brine with 0-50 mg/l (solids) scale inhibitor.
    2. Store in capped 4-oz. jar in rolling oven at 70°C for 16 hours.
    3. Remove sample, filter through 0.45-µm Millipore filter, determine Ca^{+2} with standard EDTA titration.

Appendix (Con't)

3. $BaSO_4$ Test

   1. Prepare supersaturated solution of $BaSO_4$ in brine containing 136 mg/l Ba^{+2} and 2500 mg/l SO_4^{-2} and 0-30 mg/l (solids) scale inhibitor.
   2. Store in capped 4-oz. jar in rolling oven at 70°C for 16, 24 or 64 hours.
   3. Remove sample, filter through 0.45-µm Millipore filter, determine concentration of Ba^{+2} using atomic absorption technique.

Calculation

$$\% \text{ Inhibition} = \frac{[M^{+2}]\text{ final}}{[M^{+2}]\text{ initial}} \times 100$$

Dispersancy Test

1. Prepare solution containing 1000 mg/l kaolin clay, 200 ppm Ca^{+2} (as $CaCO_3$), and 0-5 mg/l scale inhibitor; adjust to pH 7.5.

2. Agitate 1 minute in Waring Blender. Transfer to 100-ml graduate. Let stand undisturbed two hours.

3. Remove top 20 ml of supernatant. Measure turbidity in nephelometric turbidity units (NTU) with standard nephelometer. Higher values indicate better dispersancy.

FDA Clearance

ACUMER™ polymers comply with the U.S. Food and Drug Administration (FDA) Food Additives regulations indicated below provided that the final formulation meets the extractive limitations and other conditions prescribed by the regulation.

Number	Regulation Title or Application	ACUMER 1000, 1020, 1100	ACUMER 1110
173.310	Boiler-water additives	X[a]	X
175.105	Adhesives	X	X
176.170	Components of paper, paperboard in contact with aqueous and fatty food	X[b]	X[b]
176.180	Components of paper, paperboard in contact with dry food	X	X

[a]Only if converted to sodium salt.

[b]Only if converted as a sodium salt as:

1. a pigment dispersant in coatings at a level not to exceed 0.25% by weight of the pigment.

a thickening agent for natural rubber coatings, provided it is used at a level not to exceed 2% by weight of the total coating solids.

General Product Handling Information

ACUMER™ 1000/ACUMER 1020 polymers can develop a slightly hazy appearance after long-term cold storage. This change in appearance is due to intramolecular hydrogen bonding, and does not impair performance. ACUMER 1000/ACUMER 1020 that has become hazy can be made clear again by warming it to 60°C or by diluting the polymer to <30% solids.

Freezing or long-term cold storage of the ACUMER polymers may cause some separation of the components. Although product performance is not impaired, it is recommended that the ACUMER polymers not be frozen in order to avoid remixing the product.

Safe Handling Information

CAUTION: CONTACT MAY CAUSE EYE IRRITATION AND SLIGHT SKIN IRRITATION

First Aid Measures

Contact With Skin: Wash skin thoroughly with soap and water. Remove contaminated clothing and launder before rewearing.

Contact With Eyes: Flush eyes with plenty of water for at least 15 minutes and then call a physician.

If Swallowed: If victim is conscious, dilute the liquid by giving the victim water to drink and then call a physician. If the victim is unconscious, call a physician immediately. Never give an unconscious person anything to drink.

Toxicity (Range-Finding Studies – Table 7)

Table 7
Toxicity and Irritation of ACUMER™ Polymers*

	ACUMER 1100	ACUMER 1110
Acute oral (LD_{50}), rats	>5 g/kg	>5 g/kg
Acute dermal (LD_{50}), rabbits	>5 g/kg	>5 g/kg
Eye irritation, rabbits	Slight	Slight
Skin irritation, rabbits	Slight	None

Aquatic Toxicity (LC_{50}-ppm)

	ACUMER 1100	ACUMER 1110
Daphnia (48 hours)	>1000	>1000
Sunfish (96 hours)	>1000	>1000
Trout (96 hours)	700	700

* Although toxicity data has not been generated for ACUMER 1000, a 1000 $\overline{M}_w$ homolog polyacrylic acid and its corresponding sodium salt has been studied in range-finding acute mammaliana and acute aquatic toxicity tests. Results of these tests (rats, oral LD_{50}); rabbit, skin/eye irritation; 48-96 hour LC_{50}'s in daphnia magna, bluegill sunfish, and rainbow trout) indicate toxicity quite similar to that generated for ACUMER 1100. Therefore, it is expected that ACUMER 1000, which has a $\overline{M}_w$ between 1000 and 4500, will have an acute toxicity profile similar to both the 1000 $\overline{M}_w$ species as well as the 4500 $\overline{M}_w$ species. For ACUMER 1020 it is expected similar toxicity results except for eye irritation. It is expected moderate eye irritation due to the low pH of our product.

ISO 9002 Certification

All ACUMER™ polymers are manufactured in an ISO-9002 certified plant.

Handling Precautions

Before using this product, consult the Material Safety Data Sheet (MSDS)/Safety Data Sheet (SDS) for details on product hazards, recommended handling precautions and product storage.

Storage

Store products in tightly closed original containers at temperatures recommended on the product label.

Disposal Considerations

Dispose in accordance with all local, state (provincial) and federal regulations. Empty containers may contain hazardous residues. This material and its container must be disposed in a safe and legal manner.

It is the user's responsibility to verify that treatment and disposal procedures comply with local, state (provincial) and federal regulations. Contact your Dow Technical Representative for more information.

Product Stewardship

Dow has a fundamental concern for all who make, distribute, and use its products, and for the environment in which we live. This concern is the basis for our product stewardship philosophy by which we assess the safety, health, and environmental information on our products and then take appropriate steps to protect employee and public health and our environment. The success of our product stewardship program rests with each and every individual involved with Dow products - from the initial concept and research, to manufacture, use, sale, disposal, and recycle of each product.

Customer Notice

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