

# Applications Technology for Carbopol<sup>®</sup>\* Polymers and Cosmetic Formulations

Noveon, Inc. introduced Carbopol<sup>®</sup> 934 polymer to the cosmetic industry in the middle 1950's. Since that time, a number of these products have been introduced. Those polymers of most interest to the cosmetic chemist have been assigned the CTFA generic names of Carbomer 934, 940 and 941. These complementary products continue to meet the exacting ever-changing demands of advanced cosmetic products because of the properties Carbopol<sup>®</sup> polymers provide.

**Safety:** A 25 year history demonstrating non-irritating, non-sensitizing use.

Elegance: Luxurious feel.

Stability: Assured shelf life and performance.

Efficiency: Effectiveness at very low concentrations.

**Microorganism Resistance:** No support for bacteria, mold, or fungus growth.

Quality: Assured, uniform performance.

**Versatility:** Performance across wide pH and viscosity ranges.

The aim of this paper is two-fold. The first is to provide a brief review of the fundamentals of Carbopol<sup>®</sup> polymers technology. The second is the application of this technology to product formulation and production.

## **Technology Overview**

All the Carbopol<sup>®</sup> polymers are dry, polyacrylic acid polymers. When first dispersed in water or other solvent, they are tightly knotted together via hydrogen bonding. At normal use levels of up to 1% (Figure 1) no significant thickening occurs until the polymers are partially neutralized with an appropriate base to form a salt. When this salt dissolves and ionizes, it swells into its most effective thickening form (Figure 2). An electronic repulsion network gives the Carbopol<sup>®</sup> polymers their efficiency (Figure 3). The Carbopol<sup>®</sup> polymers are usually only partially neutralized since complete sodium hydroxide neutralization, for example, would produce a pH in excess of 10.

All of the Carbopol<sup>®</sup> polymers operate via the same mechanism but each has its own attributes. Note, for example, the difference in viscosity development (Figure 4). Here, the polymers have been neutralized to pH 7 with sodium hydroxide.

In addition, the optimum pH operating range varies somewhat with the Carbopol<sup>®</sup> polymer (Figure 5). Note that with Carbopol<sup>®</sup> 940, the optimum pH operating range is from 3 to 11. Curves for the other Carbopol<sup>®</sup> polymers are similar in shape but of different values.

A more appropriate description of Carbopol<sup>®</sup> polymer performance would be as flow control agents. The reason for this is that once swollen, they generate

#### Figure 1

Schematic Depicting Molecule of Carbopol<sup>®</sup> Polymer in Relaxed State





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#### Figure 2 Schematic Depicting Molecule of Carbopol® Polymer in Uncoiled State



Figure 3 Effect of pH on Viscosity of a 0.5% Solution of Carbopol® Polymer in Water



plastic flow systems and these systems exhibit the rheological property of Yield Value. Yield Value can be defined as an initial resistance to flow under applied stress. It is this property that elevates the Carbopol<sup>®</sup> polymers above mere thickeners.

The importance of Yield Value in stabilizing emulsions and suspensions is that Yield Value is an opposing force to the gravitational movement of the dispersed phase and Yield Value accompanies viscosity generation with the Carbopol<sup>®</sup> polymers. In addition to stabilizing emulsions and suspensions from separation, it provides freeze-thaw stability as well.





Figure 5 Effect of pH on Viscosity of a 1.0% Solution of Carbopol<sup>®</sup> Polymer in Water



An important point is that Yield Value imparts stability without the need for overwhelming viscosity. The gravitational pull on a suspended particle is directly proportional to the square of its diameter, (when the particles approach molecular size) the difference in specific gravities of the continuous and dispersed phases, and inversely proportional to the viscosity.

Selection of the proper Carbopol<sup>®</sup> polymer is simplified by the following table.

# Selecting the Right Carbopol<sup>®</sup> Polymer

	Rec	ommendec
<u>Requirement</u>	<u>Carbopo</u>	ol <sup>®</sup> Polyme
Clear gels > 3000 cP		940
Suspensions or emulsions at >	3000 cP	934, 940
Suspensions or emulsions at < 2	3000 cP	941
Higher shear resistance		934, 940
Better ion resistance		941
Better thermal stability		934, 940

\*Brookfield, 20 rpm, viscosities

## Neutralization

Having chosen a candidate polymer, one then asks what neutralizing agent (base) to employ. Sodium or ammonium hydroxide, are useful as well as a variety of amines. Historically, alcoholic amines, such as triethanolamine, with low odor and color have been favored. Amines pose no threat of over-neutralization (with the subsequent viscosity loss) that is possible with alkali-metal hydroxides. Lower molecular weight amino acids, as neutralizing agents, form interesting Carbopol<sup>®</sup> polymer salts due to their moisturizing contribution.

Recent concerns about nitrosamine-forming agents in cosmetics has stimulated a search for alternative neutralizing agents. Quadrol (BASF-Wyandotte) may be suitable. Quadrol is a very interesting neutralizing agent. It is useful in all-water or alcohol-water systems containing up to 50% alcohol. As with any material, one should contact the supplier concerning toxicological considerations.

Other valuable characteristics of these versatile Carbopol<sup>®</sup> polymer products are often overlooked or poorly appreciated. Let's consider the whole Carbopol<sup>®</sup> polymer character.

#### **Acidic Nature**

The Carbopol<sup>®</sup> polymers are polyacrylic acids. This means they are very hydrophilic. Secondly, the Carbopol<sup>®</sup> polymers are anionic products that will normally react with any cations. The cations of neutralizing bases are well known to form a salt of the polymer. It is not always appreciated that cationic conditioning agents can also react with, and precipitate, the Carbopol<sup>®</sup> polymers.

As acid products, just how acidic are the Carbopol<sup>®</sup> polymers? The following table shows the ionization constants of several mild acids contrasted with that of Carbopol<sup>®</sup> 934:

<u>Acid</u>	Ionization Constant
Citric	75000 X 10-7
Acetic	1800 X 10-7
Carbonic	4.5 X 10 -7
Carbopol <sup>®</sup> 934	1.6 X 10 -7

If ionization constant is considered a reasonable measure of acid strength, then the Carbopol<sup>®</sup> polymers are extremely mild. Nevertheless, they are active anions and will be sought by any cations in the system.

### **Colloidal Nature**

It is quite likely that each particle of Carbopol<sup>®</sup> polymer is an individual molecule - a kind of three dimensional, hydrophilic network about 2 to 4 microns in diameter, i.e., super colloids. Many studies have confirmed that these swollen particles display a significant electrical charge, especially after neutralization, and attract each other. This particle to particle attraction explains Yield Value.

It is then easy to visualize the well-known shear recovery displayed by all the Carbopol<sup>®</sup> polymer systems. The application of shear separates the particles, but they are rapidly snapped back together by electronic attraction upon shear release. For optimum Carbopol<sup>®</sup> polymer service, consider the influence of any ingredients, such as salts or extraneous cations in the formula, that reduce this attraction, and hence, the Carbopol<sup>®</sup> polymer's viscosity and Yield Value.

Looking at the total Carbopol<sup>®</sup> polymer character then, one can assure success in employing these high-polymer, base-actuated, hydrophilic, colloidal, flow control agents.

#### **Technology Application**

A company was producing a cream shampoo, thickened with Carbopol<sup>®</sup> 934, containing sodium lauryl sulfate (SLS). Suddenly, without a formulation or equipment change, the production viscosities went out of specification.

The problem? An aggressive buyer had purchased a cheaper grade of SLS containing a higher level of sodium sulfate. This ionic material was reducing the Carbopol<sup>®</sup> polymer's swelling capability. To correct the problem was easy: return to the original SLS. A slight increase in Carbopol<sup>®</sup> polymer level could also have solved the problem.

Frequently, order of addition, and/or choice of neutralizing agent, can avoid an interfering reaction. Water-based zinc oxide ointments have been successfully produced with Carbopol<sup>®</sup> polymer products for years. However, care is necessary. A dispersion

of zinc oxide, water, Carbopol<sup>®</sup> polymer and sodium hydroxide quickly turns to a lumpy, cottage cheese consistency. Carbopol<sup>®</sup> polymer will have its cation, and the zinc oxide offers a swamping concentration.

If one considers order of addition and neutralizer selection, success is possible. By first neutralizing the Carbopol<sup>®</sup> polymer dispersion to a pH greater than 7.2 (with a strong base such as sodium hydroxide) and then adding the zinc oxide, a mixed, sodium-zinc half salt forms which results in a smooth, stable ointment.

But many times, an interaction expresses itself much more subtly.

Hair Setting Gel				
_	<u>% By Weight</u>			
PVP or protein film former	2			
Water	q.s. 100			
Triethanolamine	0.5			
Carbopol <sup>®</sup> 940	0.5			
Disodium EDTA	0.005			
UV Absorber	0.005			
Methyl paraben	0.1			
Propyl paraben	0.1			
Color	q.s.			
Perfume	q.s.			
Solubilizer	q.s.			

If one neglects the fact that Carbopol<sup>®</sup> 940 is a high-polymer, acidic colloid, one is likely to disperse it with all the other ingredients in the water, and add the TEA as the last step. A smooth, stable gel will form if this is done.

However, polyvinylpyrrolidone (PVP) and protein film formers are somewhat cationic and flocculate the Carbopol<sup>®</sup> polymers. This flocculation is reversed upon addition of the TEA, but gel clarity is frequently adversely affected.

To avoid this interaction, either neutralize the Carbopol<sup>®</sup> polymer dispersion before addition of the PVP or protein or add the TEA combined with the PVP or protein.

Note in this formulation the use of Di-sodium EDTA and a UV absorber. Unprotected, clear, Carbopol<sup>®</sup> polymer gels, packaged in clear containers and exposed

to light, gradually lose viscosity; and the loss is permanent. Generally, this can be effectively inhibited with the use of one percent Di-sodium EDTA plus one percent UV absorber, with both percentages based on the weight of the Carbopol<sup>®</sup> polymer present. This stabilization is normally unnecessary in Carbopol<sup>®</sup> polymer products such as creams and lotions.

#### **Sparkling Sunscreen Lotion**

This formulation can be easily handled because there is no significant interaction of the actives with the Carbopol<sup>®</sup> polymer and the ethanol offers simple addition.

#### Sparkling Clear Sunscreen Lotion

Ingredients	Parts Parts
Ethanol	16.0
H2O	50.0
Carbopol <sup>®</sup> 941	1.0
Arlamol E <sup>(1)</sup>	20.0
Amerscreen P <sup>(2)</sup>	10.0
Brij-98 <sup>(3)</sup>	1.0
Quadrol <sup>(4)</sup> (50% water solution)	2.0
Brookfield Viscosity, cps	2,630

<sup>(1)</sup> Arlamol E	ICI America
(2) Amerscreen P	Amerchol
<sup>(3)</sup> Brij-98	ICI America
(4) Quadrol	BASF/Wyandotte

Rather than disperse the Carbopol<sup>®</sup> polymer in the water or add stock Carbopol<sup>®</sup> polymer dispersion, add, with stirring, the Carbopol<sup>®</sup> polymer to the alcohol (a dump-in procedure). Then add all the other actives. When these are evenly dispersed, add the water. This results in a thin, easily stirred dispersion. Add the Quadrol last to produce thickening.

This procedure minimizes air entrapment and simplifies production. This level of sunscreen usually protects the Carbopol<sup>®</sup> polymers, but should unacceptable viscosity loss occur, addition of Disodium EDTA should be considered.

### **Beating Bubbles**

Sometimes bubble content in a clear gel Carbopol<sup>®</sup> polymer system must be controlled to satisfy marketing goals. The goal may be zero bubbles or, again, "just the right amount" to add visual appeal. The two major sources of bubbles are from mechanical entrapment and chemical generation.

Minimize mechanical bubble formation by careful dispersion of the Carbopol<sup>®</sup> polymers and by arranging for air bubble release before neutralization. In

simple systems, this can be handled by allowing the dispersion to stand. In sophisticated systems, vacuum de-aeration (or even vacuum mixing) readily eliminates bubbles.

Another method to control bubble inclusion is to avoid disturbing the gel-air interface. Even slow speed mixers, that break the gel surface mechanically, incorporate air. Be certain impellers are large, low speed sweep types that are entirely submerged. Such systems should slowly turn over the gel and can de-aerate in the process. Filling equipment must be flooded, purged of air, and kept flooded to avoid air inclusion. Look to the packings on a piston tuber, for example, to avoid air injection.

A frequent cause of bubbles, especially myriads of tiny ones, is neutralizer that has become carbonated upon exposure to air. When added to the acidic Carbopol<sup>®</sup> polymer dispersion, the  $CO_2$  is liberated. To avoid this, store neutralizing agents in closed containers. On a production basis, careful inventory rotation of the neutralizer can minimize the problem.

# Conclusion

Carbopol<sup>®</sup> polymer products have complexities that contribute to their ultimate performance. An understanding of these complexities assures the professional chemist successful production formulation, production and performance.

Many of the listed ingredients may require special handling. It is the user's responsibility to obtain and follow the current recommendations and safety precautions of the individual additive supplier.

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