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Formulating Toothpaste Using Carbopol®* Polymer

Carbopol® Polymers in Toothpaste Applications

Carbopol® polymers are crosslinked polyacrylates that have found broad usage as rheology modifiers in a wide range of personal care and pharmaceutical applications. This Bulletin explores the use of Carbopol® polymers in toothpaste applications.

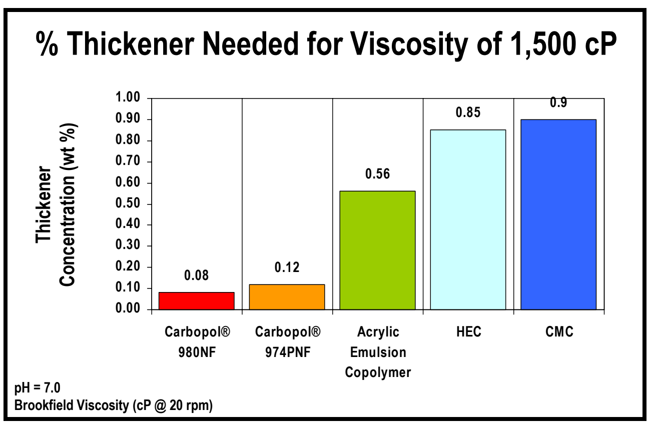
These polymers impart several desirable characteristics to toothpaste formulations:

- Viscosity
- Yield Value
- Low Thixotropy
- Clarity

Carbopol® polymers are highly efficient, imparting these properties at low concentrations. (See Figure 1.) The combination of Carbopol® polymers' ability to build yield value with low thixotropy provides for a clean, non-stringing ribbon of toothpaste coming out of the tube. From aesthetic and practical perspectives, this means that toothpaste formulations based on Carbopol® polymers:

- are pumpable
- leave minimal solids residue on the tube rim
- stand up well on the brush
- can be used to make clear gels

Figure 1: The high thickening efficiency of Carbopol® polymers can be cost effective



Carbopol® polymers also outperform natural thickeners in yield value capability. Yield value is required to suspend non-soluble additives such as actives or particles as well as debris loosened during brushing. The swollen microgel structure of Carbopol® polymers is the key element providing the prominent suspending performance in the product. Carbopol® polymers suspend various insoluble ingredients in the toothpaste system and contribute to the system's stability. Figures 2 and 3 show the comparison data of Carbopol® polymers to other natural thickeners.

Figure 2: Yield value comparisons of various thickeners in water

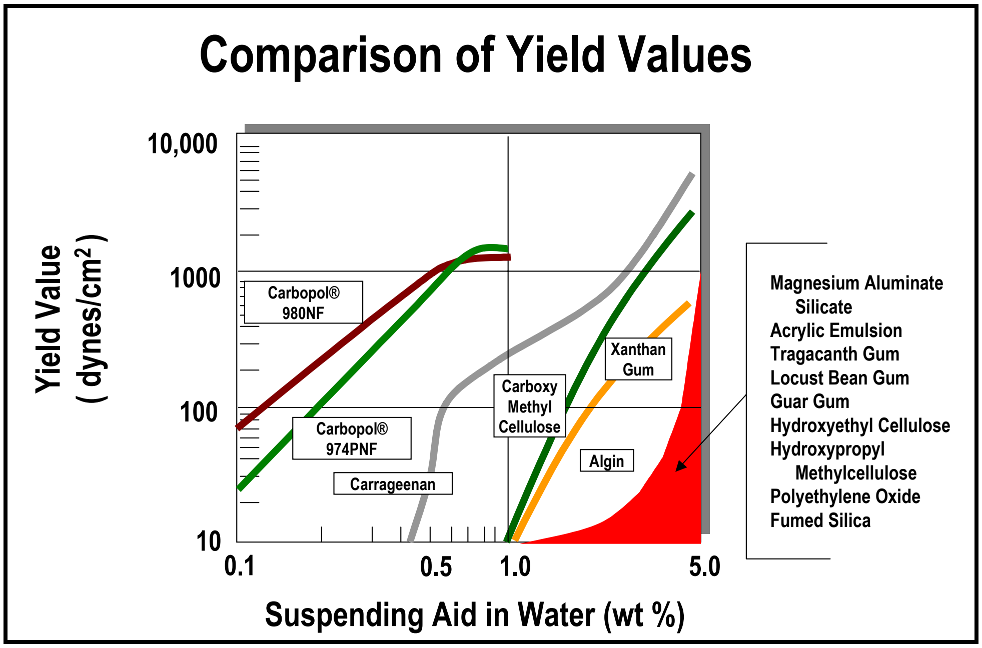
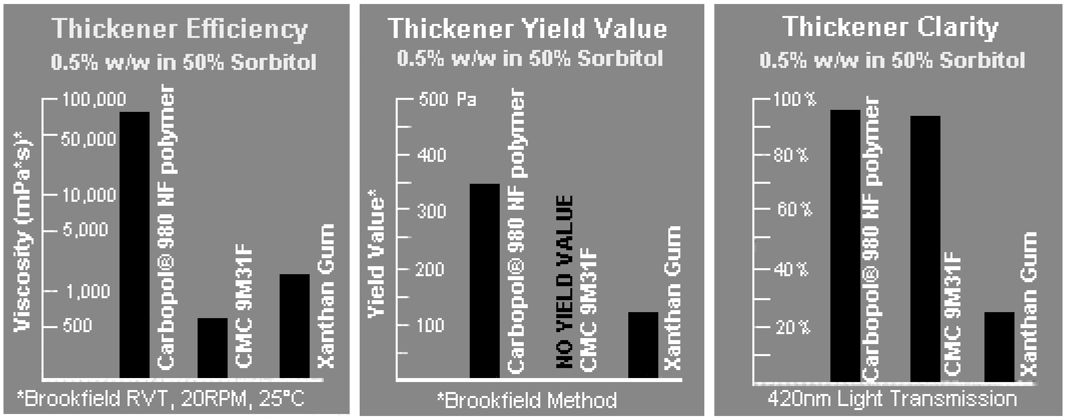


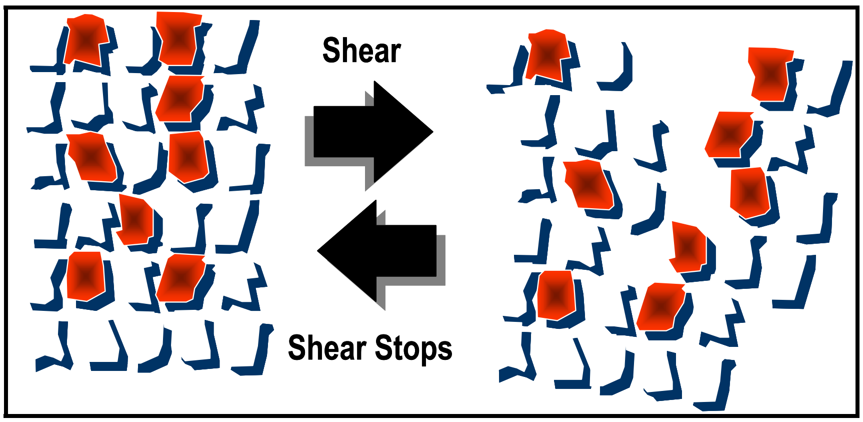
Figure 3: Efficiency and clarity comparisons at constant use level



As well as being efficient thickeners and binders, Carbopol® polymers deliver the added benefit of bioadhesion. Carbopol® polymers can be used to aid in the adhesion and delivery of dental formulations such as whitening and desensitizing treatments to the teeth. There are several publications describing how Carbopol® polymers help to enhance the bioavailability of active ingredients such as fluoride in oral care applications. (See Ref. 14 - 17.)

The microgel structure of Carbopol® polymers also imparts a shear-thinning property to the system. When a shear force is applied (squeezing the tube), the microgel structure flows like a liquid. After the shear force is removed, (stop squeezing the tube) the original high viscosity is recovered quickly, as pictured in Figure 4. Carbopol® polymer-containing gels exhibit little or no thixotropy.

Figure 4: Carbopol® polymer systems are viscoelastic. After shear is removed, the original structure recovers quickly.



High clarity products are routinely made using Carbopol® polymers in the personal care and pharmaceutical industries. This is another reason why these polymers are key ingredients in many gel-type toothpastes and transparent oral care products.

Commercial Use of Carbopol® Polymers

Carbopol® polymers are used in an array of successful toothpaste products, from regular toothpastes and gels to desensitizing and whitening products. The following table illustrates only a small sampling of commercial toothpaste containing various grades of Carbopol® polymers.

Table 1

Commercial Toothpastes Containing Carbopol® Polymers

Manufacturer	Brand Name	Product
Procter & Gamble	Gleem®	Anticavity Toothpaste
	Crest®	Cavity Protection Anticavity Toothpaste
		Tartar Protection Anticavity Toothpaste
		Whitening Plus Scope Fluoride Anticavity Toothpaste
		Dual Action Whitening Fluoride Anticavity Toothpaste
		Rejuvenating Effects Fluoride Anticavity Toothpaste
		Baking Soda & Peroxide Whitening Toothpaste
		Whitening Expressions Fluoride Anticavity Toothpaste
		Vivid White Fluoride Toothpaste
Colgate	Simply White®	Advanced Whitening Fluoride Toothpaste
		Clear Whitening gel
		Night Clear Whitening Gel
Gillette	Rembrandt®	Plus™ Premium Whitening Toothpaste with Fluoride
	Oral-B®	Stages™

Regulatory Considerations

From a regulatory perspective, food or pharmacopoeial grade ingredients are preferable, and in many cases required, for oral care applications. Lubrizol's pharmaceutical grade polymers (labeled "NF") are manufactured under current Good Manufacturing Practice (cGMP) to assure purity, consistency and quality.

Lubrizol NF grade polymers meet various current global monographs including those of the United States Pharmacopoeia/National Formulary, the European Pharmacopoeia and the Japanese Pharmaceutical Excipients Handbook[1]. These polymers are completely synthetic and therefore have no TSE/ BSE concerns associated with them.

[1] Based on customer request, Lubrizol certifies select lots of product against the JPE Carboxyvinyl Polymer Monograph

Toothpaste Composition and Ingredient Functionality

Typical toothpaste formulations contain many if not all of the following components:

- Abrasive
- Humectant
- Surfactant
- Binder
- Sweetener/Flavor/Aroma
- Active Therapeutic Ingredients
- Preservatives
- Water

The abrasives found in toothpaste function as polishing agents aiding the physical brushing during application. Abrasives also participate secondarily in the building of toothpaste rheology. Commonly used toothpaste abrasives include silica, calcium carbonate and calcium phosphates.

Polyols such as sorbitol, xylitol, and glycerin improve consistency and serve as humectants that prevent moisture loss from toothpaste formulations. Sorbitol and xylitol have the additional function of acting as secondary or in some cases primary sweeteners.

The surfactant, typically sodium lauryl sulfate, acts as a foaming agent, although many toothpastes include sodium lauroyl sarcosinate and cocamidapropyl betaine. The foaming action facilitates the removal of debris from the oral cavity.

Binders control/modify toothpaste rheology, i.e. viscosity, yield value and thixotropy. Carbopol® polymers function as highly efficient toothpaste binders, which enable low solid formulations over a broad range of viscosities. Often binders are used in combination to achieve a desired toothpaste consistency. Examples of other commonly used binders are natural gums (e.g. carageenan), carboxymethyl-cellulose, and xanthan.

Sweeteners and flavor such as sodium saccharin and flavor oils impart a pleasant initial flavor and aftertaste. Depending on regional preferences, flavor and sweeteners used in toothpaste formulations can vary greatly.

Active ingredients traditionally include anti-caries and anti-tartar agents. Sodium fluoride, stannous fluoride, and sodium monofluorophosphate are commonly used anti-caries agents. Recently, bleaching, de-sensitizing, enzymatic, and anti-microbial active ingredients have become more common in toothpaste product line extensions as well as base brands.

Compatibility of Ingredients

Carbopol® polymers are often successfully used in toothpaste formulations with xanthan gum and silica. This combination builds viscosity synergistically and the silica also acts as the abrasive.

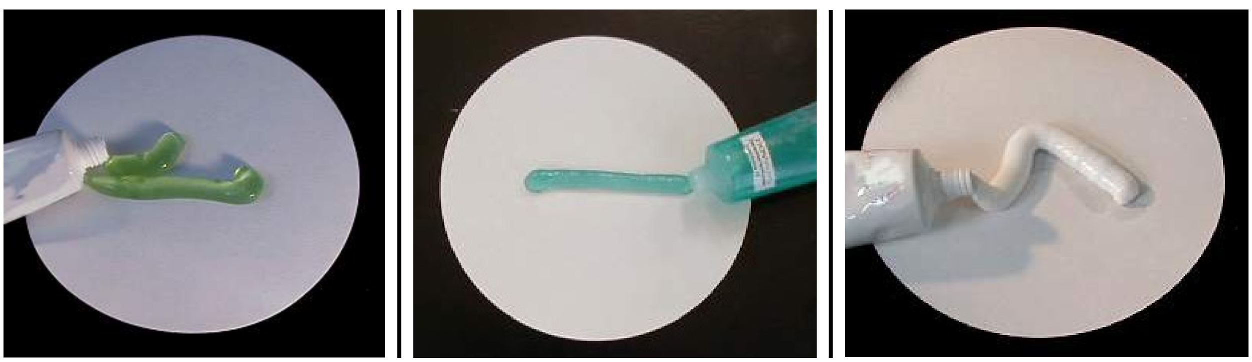
In various products, calcium carbonate is used as the abrasive rather than silica. In these formulations, Carbopol® polymers have until now not been compatible and have formed coagulates. A recent breakthrough (patent pending) has shown that using a small amount (<0.1%) of Cassia gum (Diagum™ CS Refined, Lubrizol Advanced Materials, Inc.) along with the Carbopol® polymer and calcium carbonate, results in a toothpaste formulation that has both a creamy smooth texture and a long shelf-stability profile. (Please see Formulation OC-004.)

The stability and the appearance of toothpaste has a significant effect on the consumer image of the product and the producing company itself. Toothpaste can normally be stored for months before reaching end users, making this an important feature to be considered. Thermal stability and compatibility with other ingredients is always a major challenge for formulators when using natural thickeners. Carbopol® polymers often help in achieving this property. See Figure 5.

Figure 5: Stability of toothpaste and tooth gels with and without Carbopol® polymers

Toothpaste formulated with Carbopol® polymer and Xanthan Gum	Toothpaste formulated with Carbopol® 980 NF polymer and CMC	Toothpaste formulated with CMC

Appearance before stability test

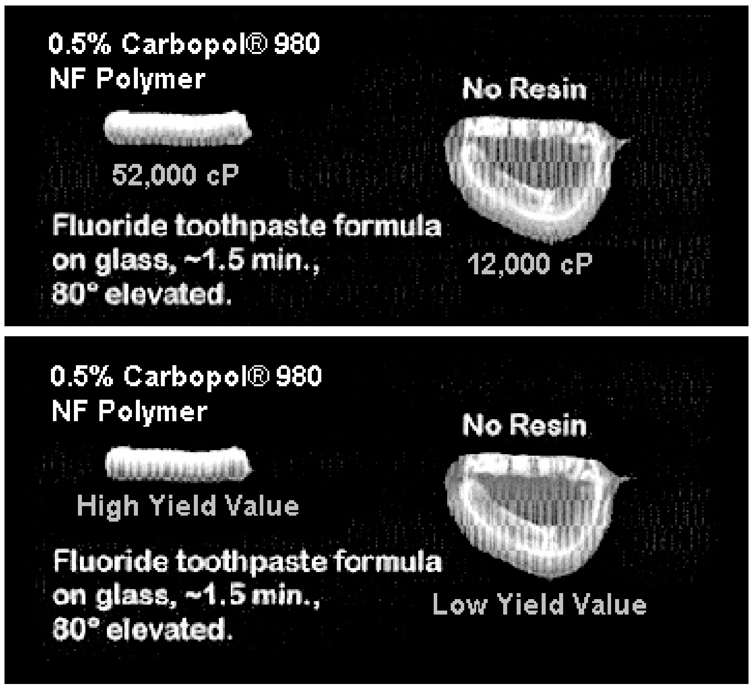


Appearance after stability test for 3 months, 45°C

Toothpaste Rheology and Consistency Control

Toothpaste texture and consistency is controlled by adjusting the binder content, as well as the solids-to-liquids and water-to-humectant ratios. Particle size and surface area of a given abrasive can affect the concentration of binder necessary to generate a specific viscosity.

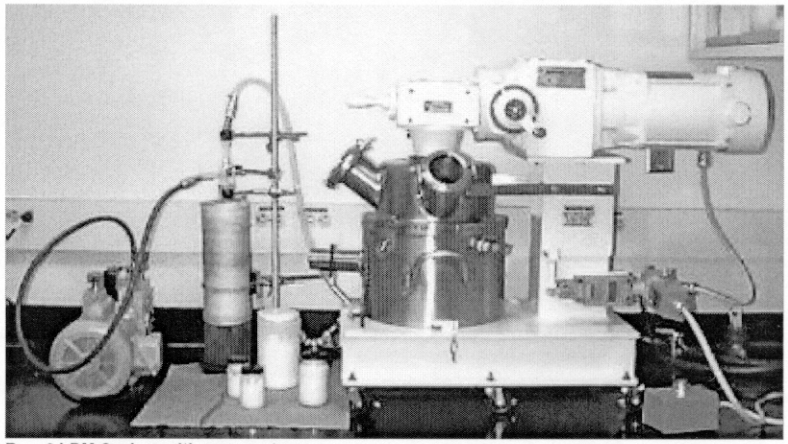
The graphics below illustrate the functionality of Carbopol® 980 NF polymer as a toothpaste binder in terms of the apparent viscosity and inherent yield value or suspending ability. The fluoride toothpaste formulation used in this example is presented at the end of this Bulletin. See Formulation OC-003.



The grade of Carbopol® polymer chosen will affect the viscosity and rheology of the finished toothpaste. The attached formulary focuses on formulations with short flow and high viscosity rheologic performance, characteristic of many commercial toothpaste products. These characteristics are intrinsic to Carbopol® 974P NF and Carbopol® 980 NF polymers. Carbopol® 971P NF and 981 NF polymers could be substituted to generate a longer flow rheology, while maintaining excellent yield value control.

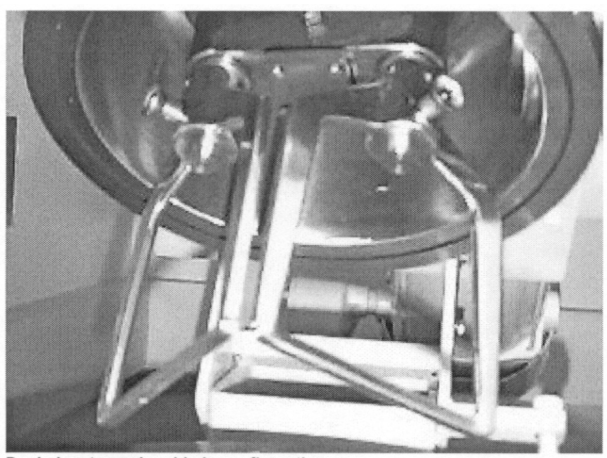
Formulating Equipment

The formulations presented in this Bulletin were developed as a 4 kilogram bench scale product using a Ross® LDM-2 mixer equipped with a vacuum trap shown below.



Ross® LDM-2 mixer with vacuum trap.

A standard dual planetary mixing blade configuration was used. This configuration is typical of industry scale-up of toothpaste formulations.



Dual planetary mixer blade configuration

The formulations in the formulary utilize an 'ambient temperature'[2] process and were tested for shelf and freeze thaw stability.

[2] OC-003 and OC-004, the clear fluoride gel formulation and the cassia formulation, utilize 80-85°C conditions to ensure hydration and full extension of the carboxymethylcellulose and the cassia gum.

Conclusions

Using Carbopol® polymers as binders in toothpaste formulations can result in an aesthetically pleasing paste or gel with low thixotropy and a high yield value. They are highly efficient and cost-effective, and are successfully used in a variety of commercially available toothpaste products including whitening, desensitizing, and baking soda with peroxide toothpastes, which demonstrates their versatility and functionality in a wide variety of formulations. Further, Lubrizol has developed new formulation technology that enables the use of calcium carbonate as a low cost abrasive with Carbopol® polymers and cassia gum to give a smooth and stable product. Calcium carbonate is a very common abrasive for regional preferences.

The first photograph below depicts the smooth spread of various toothpaste formulations. Several of the products shown; Crest®, Oral B®, Sensodyne® and Rembrandt®, contain Carbopol polymers with silica while the others to the left side contain calcium carbonate as the abrasive with other rheology agents. The top center tube is the Lubrizol starting formulation containing Carbopol® polymer, calcium carbonate and cassia gum. It has comparable rheology and mouth feel and is stable.

The photograph below shows a variety of toothpaste and other tooth whitening products that contain Carbopol® polymers and various forms of hydrogen peroxide or peroxide generating compounds.

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Fluoride Gel Toothpaste (OC-001)

Formulation:

Ingredients	% by Weight	Function
Sorbitol (70%)	43.00	Humectant / Sweetener
Deionized Water	30.17	Diluent
Silica	14.50	Abrasive
Glycerin	9.60	Humectant
Sodium Lauryl Sulfate (30%)	1.00	Surfactant
Sodium Monofluorophosphate	0.75	Anti-Caries Agent
Xanthan Gum	0.43	Binder
Carbopol® 974P NF Polymer	0.35	Binder
Sodium Saccharin	0.20	Sweetener
Flavor / Color	q.s.	
TOTAL	100.0	

Properties:

Appearance	Translucent Gel
Viscosity, cP[3]	28,000
pH[4]	~5.3
Stability (4 weeks 45°C)	Pass

NOTE: The viscosity of the formulation and the pH may be adjusted upward with the addition of a neutralizing base. NaOH (18%) additions, and/or Na_3PO_4 to a pH of ~ 7.4 show an increase in viscosity to ~70,000 cP.

[3] Brookfield RVT, 25°C, 20 rpm, #7
[4] 10% solution in DI water

Fluoride Gel Toothpaste (OC-001)

Procedure:

1. Disperse Carbopol® polymer into the water. Mix slowly for ~15 minutes to hydrate.

2. Pre-wet xanthan gum into glycerin and then hydrate with sorbitol (70% aqueous solution). Mix well for ~15 minutes to thicken and smooth the dispersion.

3. Combine Carbopol® polymer and xanthan gum dispersions and mix ~10 minutes until smooth and homogenous.

4. To the combined phases add the sodium monofluorophosphate and sodium saccharin. Mix well ~10 minutes under 27in. Hg vacuum to remove entrapped air.

5. Add silica. Mix slowly for 1 minute to incorporate the abrasive into the gel base. Mix more rapidly under 27 in. Hg vacuum to disperse the silica.

6. Transfer the sodium lauryl sulfate surfactant with any color and flavor to the mixing vessel. Mix at low speed under 27 in. Hg vacuum until homogeneous.

Comments:

If local regulations allow use of a non-oral pharmaceutical grade, Carbopol® 980 NF polymer or Carbopol® 956 polymer can be substituted for Carbopol® 974P NF polymer with minimal effect on the formulation properties.

Tartar Control Toothpaste (OC-002)

Formulation:

Ingredients	% by Weight	Function
Sorbitol (70%)	42.85	Humectant / Sweetener
Deionized Water	27.42	Diluent
Silica	14.50	Abrasive
Glycerin	9.60	Humectant
Tetrapotassium Pyrophosphate	2.90	Anti-Tartar Agent
Sodium Lauryl Sulfate (30%)	1.00	Surfactant
Sodium Monofluorophosphate	0.75	Anti-Caries Agent
Xanthan Gum	0.43	Binder
Carbopol® 974P NF Polymer	0.35	Binder
Sodium Saccharin	0.20	Sweetener
Flavor / Color	q.s.	
TOTAL	100.0	

Properties:

Appearance	Translucent Gel
Viscosity, cP[5]	63,000
pH[6]	~7.8
Stability (4 weeks 45°C)	Pass

[5] Brookfield RVT, 25°C, 20 rpm, #7
[6] 10% solution in DI water

Tartar Control Toothpaste (OC-002)

Procedure:

1. Disperse Carbopol® polymer into the water. Mix slowly for ~15 minutes to hydrate.
2. Add the tetrapotassium pyrophosphate to the polymer dispersion and mix well.
3. Pre-wet xanthan gum with glycerin and then hydrate with sorbitol (70% aqueous solution). Mix well for ~15 minutes to thicken and smooth the dispersion.
4. Combine Carbopol® polymer and xanthan gum dispersions and mix ~15 minutes until smooth and homogenous.
5. To the combined phases add the sodium monofluorophosphate and sodium saccharin. Mix well ~10 minutes under 27in. Hg vacuum to remove entrapped air.
6. Add silica. Mix slowly for 1 minute to incorporate the abrasive into the gel base. Mix more rapidly under 27 in. Hg vacuum to disperse the silica.
7. Transfer the sodium lauryl sulfate surfactant with any color and flavor to the mixing vessel. Mix at low speed under 27 in. Hg vacuum until homogeneous.

Comments:

If local regulations allow the use of a non-oral pharmaceutical grade, Carbopol® 980 NF polymer or Carbopol® 956 polymer can be substituted for Carbopol® 974P NF polymer with minimal effect on the formulation properties.

Clear Fluoride Gel Toothpaste (OC-003)

Formulation:

Ingredients	% by Weight	Function
Sorbitol (70%)	68.73	Humectant / Sweetener
Deionized Water	9.52	Diluent
Carbopol® 980 NF Polymer	0.50	Binder
Carboxymethylcellulose 9M31F	0.50	Binder
Sodium Hydroxide (18%)	0.80	Neutralizer
Sodium Monofluorophosphate	0.75	Anti-Caries Agent
Sodium Saccharin	0.20	Sweetener
Zeodent® 113 Silica	15.00	Abrasive
Sodium Lauroyl Sarcosinate	2.00	Surfactant / Foaming Agent
Flavor / Color	q.s.	
TOTAL	100.0	

®Zeodent is a registered trademark of the J. M. Huber Corporation.

Properties:

Appearance	Clear Gel
Viscosity, cP[7]	70,000 - 80,000
pH[8]	~6.0
Stability (4 weeks 45°C)	Pass
Specific Gravity	1.3

[7] Brookfield RVT, 25°C, 20 rpm, #7
[8] 10% solution in DI water

Clear Fluoride Gel Toothpaste (OC-003)

Procedure:

1. Combine ~38 parts of sorbitol with ~3.5 parts of water.
2. Disperse the CMC 9M31F into the sorbitol solution. Disperse Carbopol® polymer into the remaining water.
3. Heat the dispersion to 80°C while mixing to insure hydration of both polymers and full extension of the CMC. When 80°C is reached, the mixture may be allowed to cool while mixing for ~20 minutes.
4. Dissolve the sodium monofluorophosphate and sodium saccharin into 5.0% of the remaining water. Add this to the polymer system and mix until full homogenous.
5. Neutralize the gel base with the sodium hydroxide (18%) allowing for complete mixing.
6. Disperse the Zeodent® 113 silica into the remaining 30% of the sorbitol (70%). Add the dispersion to the neutralized gel base. Mix at medium speed to fully incorporate the dispersion.
7. Add the sodium lauroyl sarcosinate surfactant, any remaining water from the process (~1.0%) and flavors or colors. Mix at medium speed until homogenous.

Special Notes:

The clarity of this dentifrice is heavily dependent on matching the refractive index (RI) of the gel base with the silica abrasive. Anything in the process that introduces changes in the water /sorbitol ratio will affect the RI of the base. At the recommended vacuum setting of 25-27 in. Hg, and the specified vacuum mixing times, the correct ratio is achieved in the finished product.

Cloudy product may indicate:

1. Incomplete hydration of the silica abrasive. This may rectify itself on standing 24-48 hours, or the initial abrasive dispersion may be heated to ~55°C before adding.
2. Too much water removal in vacuum processing. Titration of a small sample of the formula with water should give the correct addition needed to clear the system. (RI of the base is too high.)

Too little water is removed in vacuum processing. Titration of a small sample of the formula with sorbitol (70%) should give the correct addition needed to clear the system. If the amount of sorbitol necessary is too great, glycerin may also be of help. If further addition of material is undesirable, the product may be mixed slowly under vacuum to remove more water.

Calcium Carbonate-Filled Toothpaste (OC-004*)

Formulation:

Ingredients	% by Weight	Function
Sorbitol (70%)	43.00	Humectant / Sweetener
Deionized Water	35.00	Diluent
Xanthan Gum, NF	0.62	Binder
Carbopol® 974P NF Polymer	0.70	Binder
Diagum® CS *Refined* Cassia	0.07	Binder
Sodium Monofluorophosphate	0.75	Anti-Caries Agent
Sodium Saccharin	0.20	Sweetener
Calcium Carbonate USP/FCC	14.50	Abrasive
Glycerin USP	4.82	Humectant
Sodium Lauryl Sulfate	0.34	Surfactant / Foaming Agent
Flavor / Color	q.s.	
TOTAL	100.0	

Properties:

Appearance	Opaque Gel
Viscosity, cP[9]	20,000 – 25,000
pH[10]	~7.6
Stability (4 weeks 45°C)	Pass
Specific Gravity	1.3

[9] Brookfield RVT, 25°C, 20 rpm, #7
[10] 10% solution in DI water

*Patent Pending

Calcium Carbonate-Filled Toothpaste (OC-004)

Procedure:

1. Cassia gum is dispersed in 22 parts water, heated to 85°C and cooled to room temperature, all with constant mixing.
2. Disperse Carbopol® polymer into the above cassia dispersion. Mix slowly for ~15 minutes to hydrate.
3. Pre-wet xanthan gum with glycerin and then hydrate with sorbitol (70% aqueous solution). Mix well for ~15 minutes to thicken and smooth the dispersion.
4. Combine Carbopol® polymer and xanthan gum dispersions and mix ~10 minutes until smooth and homogenous.
5. Dissolve the sodium monofluorophosphate and sodium saccharin in the balance of the water, and add to the mixture. Mix well ~10 minutes under 27in. Hg vacuum to remove entrapped air.
6. Add calcium carbonate. Mix slowly for 1 minute to incorporate the abrasive into the gel base. Mix more rapidly under 27 in. Hg vacuum to disperse the calcium carbonate.
7. Transfer the sodium lauryl sulfate surfactant with any color and flavor to the mixing vessel. Mix at low speed under 27 in. Hg vacuum until homogeneous.

Comments:

If local regulations allow use of a non-oral pharmaceutical grade, Carbopol® 980 NF polymer or Carbopol® 956 polymer can be substituted for Carbopol® 974P NF polymer with minimal effect on the formulation properties.

The above recipe has been prepared at laboratory scale without the heating step in Procedure item #1; it gave a similar product which was also stable to both thermal and freeze-thaw challenge, but this has not been confirmed by further scaleup to large quantities.