BULLETIN VC-806A (Supersedes VC-806)

Plasdone™ K-29/32 polymer

A non-oxidative, non-abrasive solution for whiter teeth

Whiter and brighter smiles

Coffee, tea, wine, dark berries and many other foods and beverages contain pigmented polyphenolic compounds that provide color in food, but also stain teeth. Plasdone K-29/32 polymer is effective in eliminating stains by binding to stains, increasing their solubility in water and effecting their removal. In vivo studies have shown that toothpaste and mouth rinses formulations with up to 2% Plasdone K-29/32 polymer show improved stain removal of black tea, Chinese black tea, red wine and coffee from artificial teeth and bovine teeth. It has also been shown in laboratory tests to provide increased whitening in formulations containing tetrasodium pyrophosphate. As Plasdone K-29/32 polymer is non-abrasive and non-oxidative it does not harm enamel or cause tooth sensitivity. Because it is non-ionic and works by a different mechanism, it can be used in combination with most other whitening approaches to improve the whitening effects of toothpaste and mouth rinses.

In addition to foods and beverages, it is well known that cationic antibacterial agents, such as chlorohexidine and cetylpyridinium chloride (CPC) as well as stannous fluoride darken teeth over time. In-vitro studies have shown that the addition of Plasdone K-29/32 polymer effectively reduces these staining effects and it is expected that noticeably whiter teeth will result.

Benefits

- Removes stains by binding to stain-causing agents
- Delivers non-abrasive teeth whitening
- Is non-oxidative
- Is globally accepted
- Works in toothpastes and mouth rinses and with other whitening approaches
- Does not wear teeth enamel or cause teeth sensitivity
- Reduces teeth staining from cationic antibacterials and stannous compounds

Applications

- Toothpastes
- Mouth rinses

Widely used polymer

Plasdone K-29/32 polymer is a pharmaceutical-grade, linear homopolymer of N-vinyl-2-pyrrolidone (VP) (Figure 1). Plasdone polymers are bioadhesive, readily soluble in water and solvents, physiologically inert, nonionic, nontoxic, temperature independent and pH stable. Historically, it was difficult to determine the molecular weight of polyvinylpyrrolidone (PVP) polymers directly. Thus, the K-value was adopted to classify

the various molecular weights of PVP polymers (Table 1). The K-value, a function of the average degree of polymerization and the intrinsic viscosity of the polymer, is calculated from the kinematic viscosity of an aqueous polymer solution.

Plasdone™ K-29/32 polymer conforms to the current USP/NF, Ph. Eur and JPE excipient monographs for povidone. It has a long history of use in pharmaceutical applications and is suitable for use in oral care products.

Figure 1
Chemical structure of Plasdone K-29/32 polymer

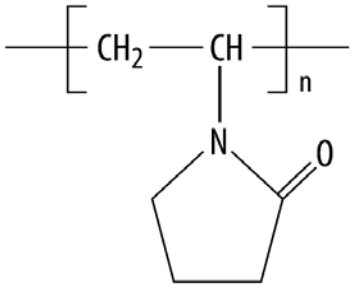


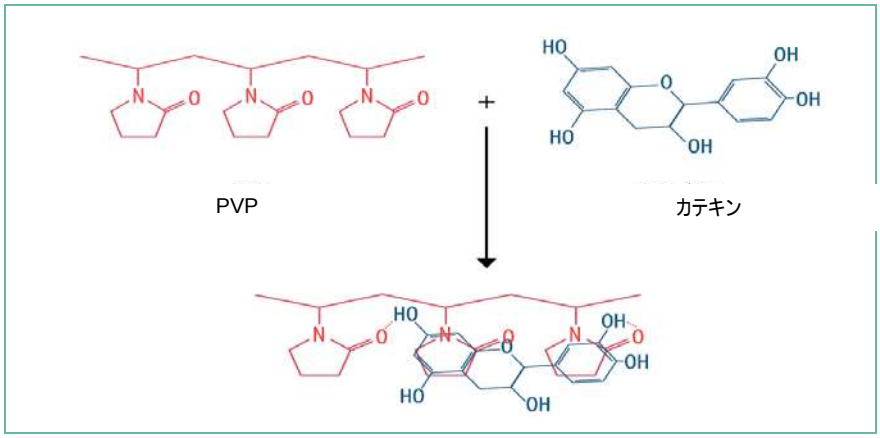
Table 1
Properties of Plasdone K-29/32 polymer

INCI Name	Appearance	K-Value	Typical Average Molecular Weight	Brookfield Viscosity at 25°C (cP)	Typical Average Particle Size (microns)	Density (g cm^{-3})
PVP	White to creamy white powder	29-32	58,000	2.5 (5% aqueous solution)	80	0.36 Bulk 0.47 Tap

Lifts staining agents to whiten teeth

Plasdone polymers form complexes with phenolics, such as catechin, via hydrogen bonding (Figure 2). The resulting complex is more soluble in water and easily removed during product use.

Figure 2
Polyvinylpyrrolidone (PVP) polymers complex with phenolics via hydrogen bonding

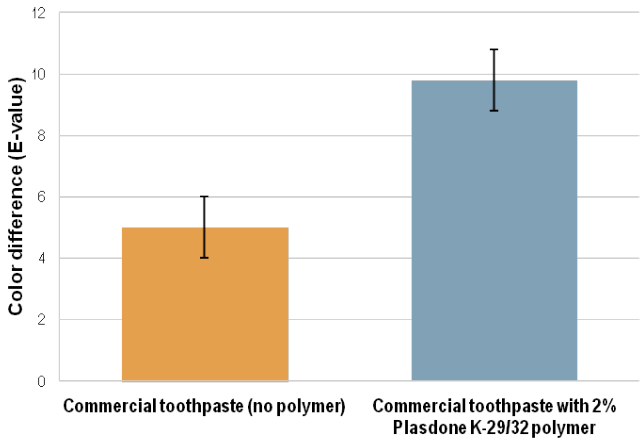


The proof is in the smile after brushing

In-vitro brushing studies have demonstrated the stain removal efficacy by the addition of Plasdone K-29/32 polymer to toothpaste. Toothpastes with Plasdone K-29/32 polymer show better stain removal after brushing without increasing the abrasivness of the toothpaste. Whitening toothpastes that contain silica and aluminum oxides can possess high abrasivity in order to remove stains; however, high abrasivity can lead to excessive tooth wear over time. Plasdone K-29/32 polymer works by a different mechanism. It can be used with abrasives and polyphosphate tartar control agents to improve the whitening effect and cleaning power of toothpastes.

In one study, 2% Plasdone™ K-29/32 polymer was added to commercial toothpaste with a radioactive dentine abrasivity (RDA) value of 105 indicating medium abrasivity. Tea-stained hydroxyapatitive (HAP) disks were brushed with the polymer-containing toothpaste and the commercial control without polymer. The results show a significant increase in color difference (ΔE) of the HAP disks compared to the control without polymer (Figure 3). The whiteness or luminosity (L-value) component of color measurement showed similar results.

Figure 3
The addition of Plasdone K-29/32 polymer improves stain removal of toothpaste without increasing abrasivity

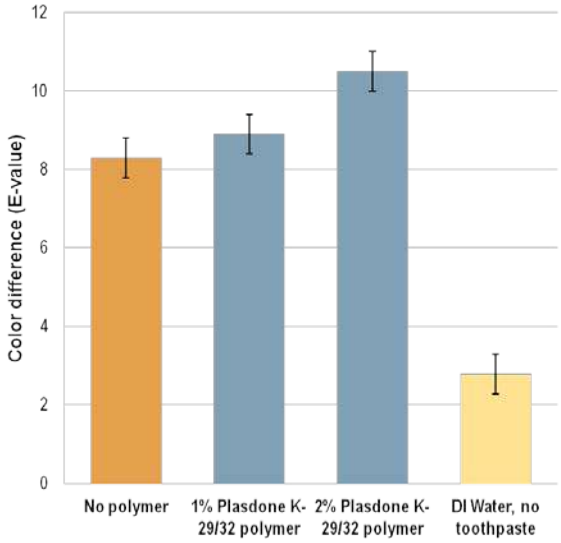


In a second study, model laboratory toothpaste without abrasives (Table 2) was formulated with 1% and 2% Plasdone K-29/32 polymer and compared to a control (without polymer). The color difference (ΔE) before and after brushing tea-stained HAP disks shows the toothpaste with 2% Plasdone K-29/32 polymer is highly effective at removing stains (Figure 4).

Table 2
Model aqueous phase toothpaste formula with Plasdone K-29/32 polymer

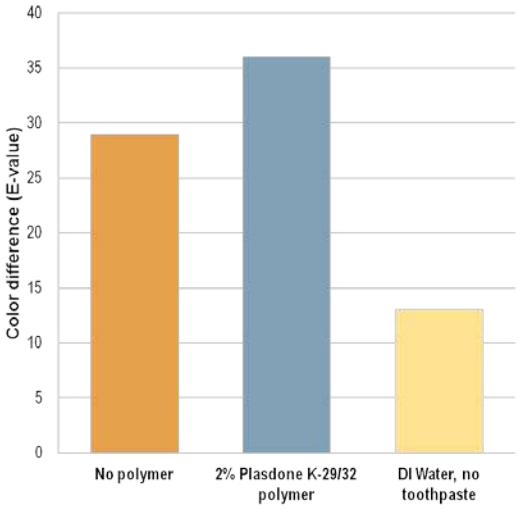
Ingredient	Use Level (% w/w)
DI Water	64.24
Sorbitol (70%)	20.00
Glycerol	13.00
Sodium lauryl sulfate	1.46
Polymer	**2.00**
Essential oil flavors	1.06
Sodium fluoride	0.24

Figure 4
Plasdone™ K-29/32 polymer at 2% use level in toothpaste shows greater removal of tea stain from HAP disks after brushing



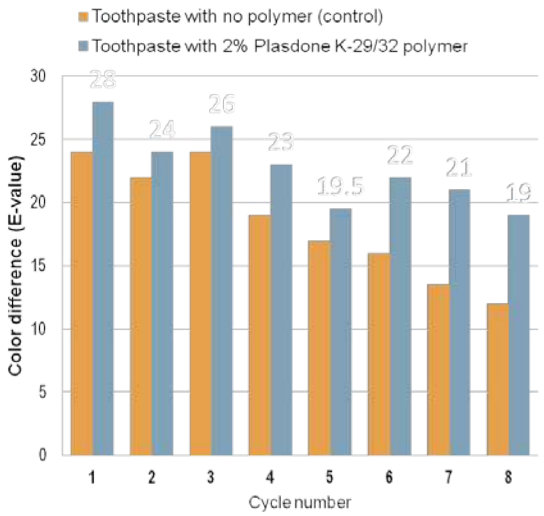
Next, brushing experiments with performed on non-vital bovine teeth stained with a combination of tea, coffee, and other staining compounds1. The results show the cleaning properties of the toothpaste formulation were significantly improved with the addition of 2% Plasdone K-29/32 polymer (Figure 5).

Figure 5
Plasdone K-29/32 polymer at 2% enhanced the cleaning properties of a model toothpaste formulation



Additional brushing studies were conducted on bovine teeth to explore the effects of repeated use of toothpaste containing Plasdone K-29/32 polymer. In this study, the bovine teeth underwent eight staining cycles, each followed by brushing cycles to show the effects over time. Color was measured after each brushing. The data show that toothpaste with 2% Plasdone K-29/32 polymer removes stains significantly better than toothpaste without polymer (Figure 6). The whiteness or luminosity (L-value) component of color measurement showed similar results.

Figure 6
Plasdone™ K-29/32 polymer reduces and prevents staining over multiple-uses



Whiter smiles after rinsing

In-vitro studies have also demonstrated the teeth-whitening effects of Plasdone K-29/32 polymer in mouth rinse (Figure 7). Plasdone K-29/32 polymer can easily be added to mouth rinse formulations to enhance cleaning properties. It is soluble in water and solvents and has low viscosity in solution.

Figure 7
The mouth rinse containing Plasdone K-29/32 polymer provided noticeably whiter results

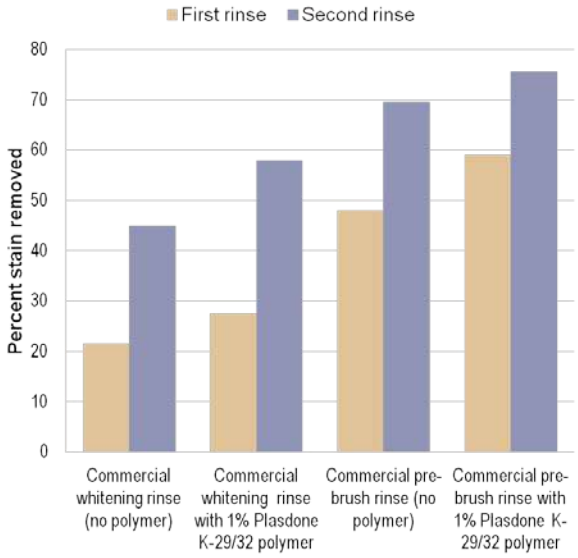
Commercial mouth rinse with 1**% Plasdone K-29/32 polymer**

Commercial mouth rinse (no polymer)

All HAP disks were immersed in mouth rinse for 5 minutes
All photos are un-retouched

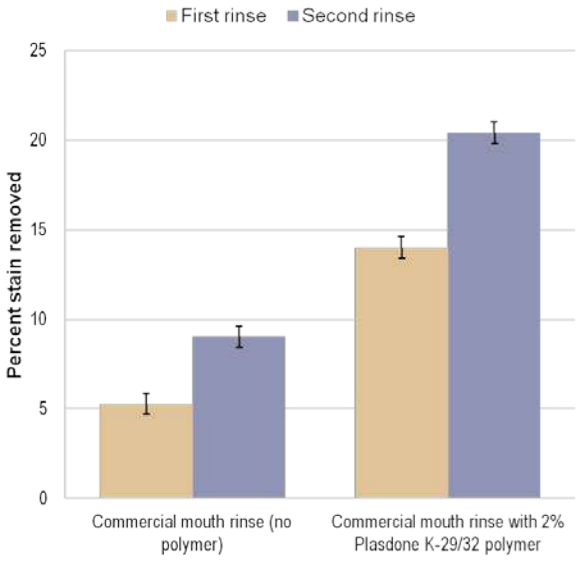
In one study, 1% Plasdone K-29/32 polymer was added to two commercial whitening mouth rinses containing approximately 2% hydrogen peroxide. The whitening performance of the mouth rinses was compared to the peroxide-rinses without polymer. HAP disks were stained with black tea and then rinsed twice for five minutes each. Instrumental color readings were taken before and after staining the HAP disks as well as before and after each rinse. The results clearly show that the addition of Plasdone K-29/32 polymer significantly improves stain removal over both of the peroxide commercial whitening rinses (Figure 8).

Figure 8
Plasdone™ K-29/32 polymer improves the stain removal of commercial peroxide-based mouth rinses



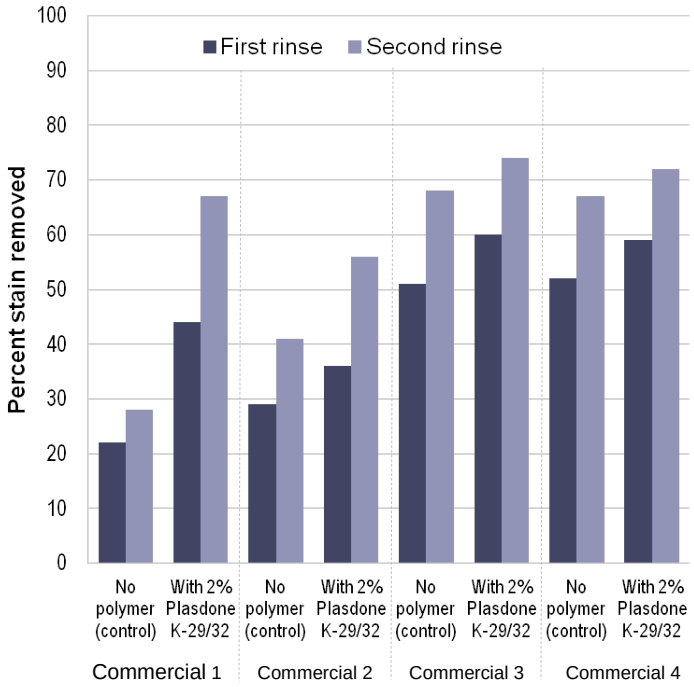
The efficacy of Plasdone K-29/32 polymer is not limited to tea stains. To show the effectiveness of Plasdone K-29/32 polymer at removing stains caused by a range of staining beverages, Chinese black tea, red wine (Shiraz) and coffee were used to stain HAP disks. Plasdone K-29/32 polymer was then added to a commercial mouth rinses and compared to the commercial product without polymer. The disks were rinsed twice for five minutes each. The results clearly show the improvements in stain removal with the addition of Plasdone K-29/32 polymer (Figures 9 to 11).

Figure 9
With the addition of 2% Plasdone K-29/32 polymer,
a commercial mouth rinse showed greater stain removal of Chinese black tea from HAP disks



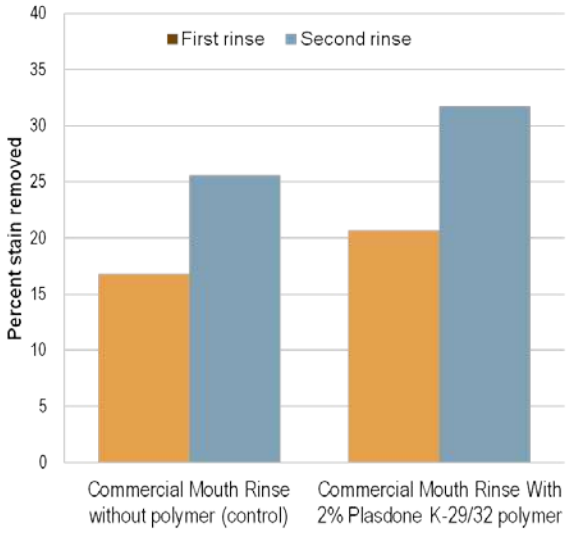
The data is the average of 8 results for each condition

Figure 10
Commercial mouth rinse with 2% Plasdone™ K-29/32 polymer shows significant removal of red wine stain versus control without polymer



The data is the average of 12 results for each condition

Figure 11
A commercial mouth rinse with 2% Plasdone K-29/32 polymer improves the removal of coffee stains from HAP over control without polymer



The data is the average of 8 results for each condition

Ashland
always solving

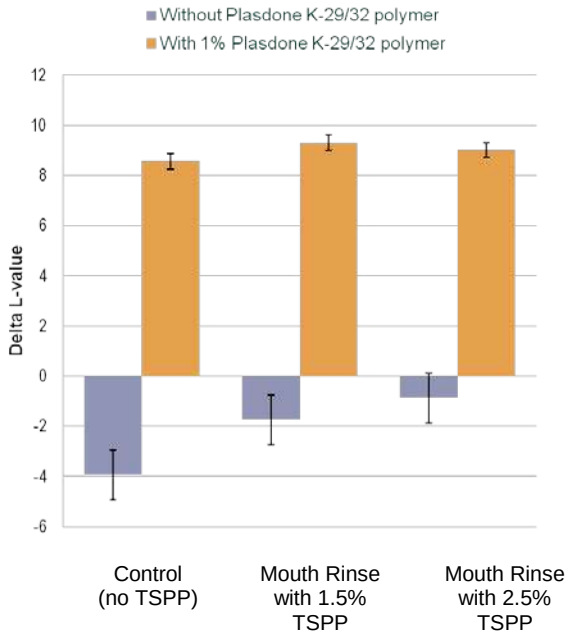
More *in-vitro* whitening than sodium pyrophosphate

Plasdone™ K-29/32 polymer appears to have a much greater in vitro whitening effect on the tea-stained HAP disks than tetrasodium pyrophosphate (TSPP) or sodium pyrophosphate, a commonly used ingredient to remove plaque. In laboratory tests, 1% Plasdone K-29/32 polymer was added to a mouth rinse formulation containing TSPP (Table 3). Luminosity or whiteness (L-value) component of color measurement was recorded after staining and after treatment with the mouth rinse for 60 minutes. The luminosity differences (delta L-values) show that tea stained HAP disks treated with the mouth rinse containing 1% Plasdone K-29/32 polymer are statistically whiter (Figure 12). Positive luminosity differences indicate the whitening effect of the rinse treatment on the stained disks while the negative luminosity differences reflect the darkening effect of the rinse treatment on the stained disk.

Table 3
Mouth rinse formulation containing TSPP

Ingredient	Use Level (% w/w)
DI Water	q.s.
Plasdone K-29/32 polymer	0 or 1
TSPP	0,1.5 or 2.5
Sorbitol (70%)	20.00
Ethanol	8.70
Benzoic Acid	0.53
Poloxamer 407	0.20
Sodium Benzoate	0.20
Sodium Lauryl Sulfate	0.20
Xanthan Gum	0.05
FD&C Blue #1	0.00038
FD&C Yellow #5	0.00031
Sodium Benzoate	0.20
Sodium Lauryl Sulfate	0.20
Xanthan Gum	0.05

Figure 12
Mouth rinse with Plasdone K-29/32 polymer shows greater whitening compared to mouth rinse with TSPP alone

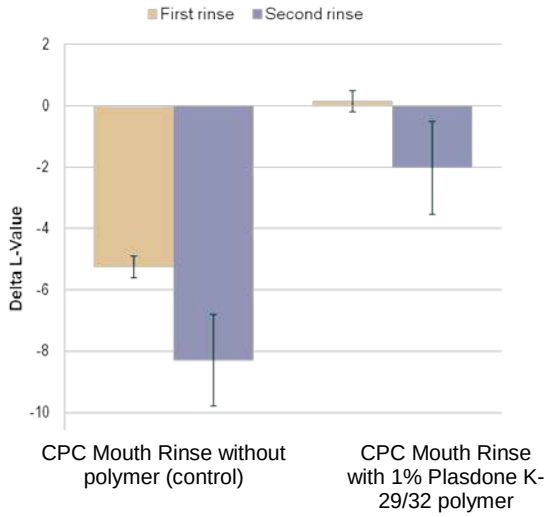


Less staining from cationic antibacterial agents

Plasdone™ K-29/32 polymer has been shown to reduce staining of HAP disks caused by cetylpyridinium chloride (CPC), a cationic antibacterial agent. It is well known that CPC and chlorohexidene gluconate (CHG) stain teeth; however, these antibacterial agents have desirable benefits as they have been shown to be effective at preventing plaque and reducing gingivitis. Thus, it is highly desirable to reduce teeth staining of mouth rinses containing CPC or CHG without reduction of antimicrobial efficacy.

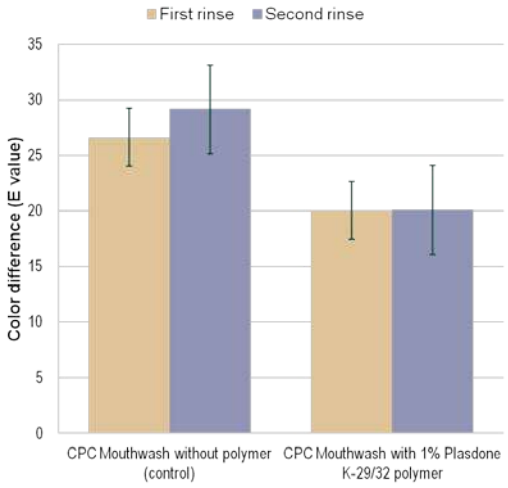
In one study, a model CPC-containing mouth rinse was evaluated with and without 1% Plasdone K-29/32 polymer on tea-stained disks. The mouth rinse formulation is shown in Table 4. In Figure 13, the luminosity differences (delta L) show that the mouth rinse with CPC significantly darkened the tea-stained disks (control). Delta L is the difference in whiteness after rinsing and before rinsing (after staining) HAP disks. Positive luminosity differences indicate the whitening effect of the rinse on the stained HAP disk while the negative luminosity differences show the rinse is darkening the stained HAP disk. The addition of 1% Plasdone K-29/32 polymer to the formulation prevented the darkening of the tea-stained discs.

Figure 13
HAP disks are whiter after treatment with CPC mouth rinse containing Plasdone K-29/32 polymer



In addition to luminosity, the color difference (ΔE) of the HAP disks compared to the control without polymer is shown in Figure 14. The results compare the color of the HAP disks after staining with the color after treatment with the model mouth rinse. A smaller color difference indicates less color change. The results show the disks treated with the CPC-containing mouth rinse with 1% Plasdone polymer were significantly lighter than the disks treated with the control mouth rinse (without polymer).

Figure 14
HAP disks show less color change when treated with CPC mouth rinse containing Plasdone™ K-29/32 polymer



The color difference values are the results of averaging 10 individual color difference results obtained from the disks in each condition

An *in-vitro* disk retention assay (DRA) method, as described in the literature, was used to evaluate the impact of Plasdone K-29/32 polymer on the efficacy of CPC in commercial mouth rinses[3]. The method is based on the binding of the cationic CPC molecule to the anionic surface of a cellulose disk. Only the available (or active) CPC binds to the disks. The in-vitro DRA method has been shown, in the literature, to correlate to in-vivo clinical results on CPC activity[4].

The results (Figure 15) show that Plasdone K-29/32 polymer has no apparent effect on the activity of CPC. Furthermore, the DRA results for Plasdone K-29/32 polymer alone in water averaged zero the same as water alone. These data show that the Plasdone K-29/32 polymer has no detrimental effect on the DRA method.

Figure 15
Plasdone K-29/32 polymer does not impact efficacy of CPC

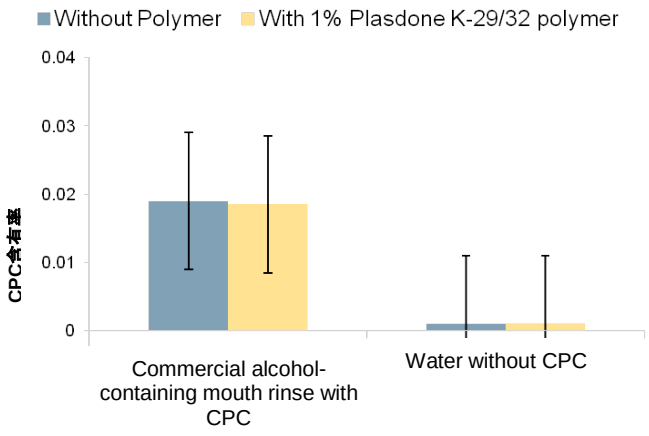


Table 4
Model alcohol-containing mouth rinse formulation with CPC

Ingredient	Use Level % w/w
Methyl salicylate (wintergreen) (1% ethanol solution)	0.0750
Menthol (1% ethanol solution)	0.0430
Methylfuran (1% ethanol solution)	0.0150
Thymol (1% ethanol solution)	0.0130
Menthone (1% ethanol solution)	0.0090
Cinnamaledhyde (1% ethanol solution)	0.0060
Eugenol (1% ethanol solution)	0.0008
Ethanol	16.0000
Glycerin	9.0000
Plasdone™ K-29/32 polymer	**0 -1.0000**
Polysorbate 80	0.1200
Sodium saccharin	0.0550
Sodium benzoate	0.0500
Cetylpyridinium chloride	0.0500
Domiphen bromide	0.0500
Benzoic acid	0.0500
FD&C Blue No. 1 (0.1% water solution)	0.00038
FD&C Yellow No. 5(0.1% water solution)	0.00031
Deionized water	73.46251-74.46251
TOTAL	**100.0000**

Less teeth staining from stannous ions

Stannous compounds, such as stannous fluoride, are used in oral care products. Stannous compounds can stain teeth due to sulfur compounds found in the mouth that react with stannous ion to form stannous sulfide. Stannous sulfide is a sticky, finely divided, yellowish-brown precipitate that is attracted to the surface of teeth resulting in teeth yellowing and darkening. Reactive sulfur compounds are released into saliva from the degradation of sulfur-containing proteins and amino acids from food and beverages. Although this stannous sulfide staining process takes months or years to become visible, it will eventually darken teeth.

An *in-vitro* test procedure for evaluating stain removal from teeth by toothpaste was modified to study the staining effects of stannous fluoride on HAP disks. For laboratory purposes, visible staining could be achieved in a few hours instead of in months or years. Typically, the artificial saliva used in the in-vitro method does not contain the enzymes found in saliva, thus it does not degrade proteins to provide the reactive sulfur compounds found in the oral cavity. For laboratory evaluation purposes, 5% sodium thiosulfate was introduced into an artificial tooth pellicle (mucin supernatant). A liquid model toothpaste was formulated to contain 4.54% stannous fluoride or 10-times the normal use level. The HAP disks were placed into the model system and incubated for 1.5 hours and then rinsed thoroughly with deionized water and allowed to dry overnight prior to color measurement.

The delta b* and delta L* values are shown in Figures 16 and 17. In CIE color space, as b* becomes larger in value, yellow becomes more intense. As b* becomes smaller, the blue component becomes more intense. B* becomes lighter, overall, as it approaches zero from either the negative or positive direction. L* or luminosity is an indication of whiteness and is measured on a scale from 0 (black) to 100 (white). Negative delta L* values represent a darkening of the color. Thus, the results (Figure 16) show that the

addition of 2% Plasdone™ K-29/32 polymer reduces the yellowing effect compared to the control without polymer. The results in Figure 17 show greater whitening with polymer compared to the control sample without polymer.

Figure 16
Plasdone K-29/32 polymer reduces yellowing on HAP disks treated with stannous fluoride containing model toothpaste

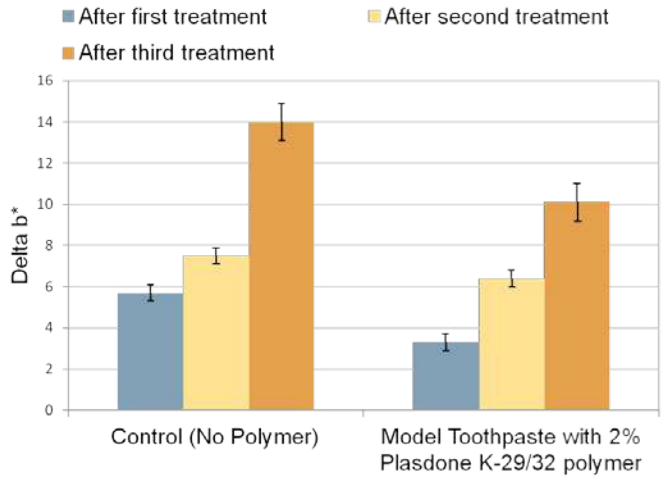
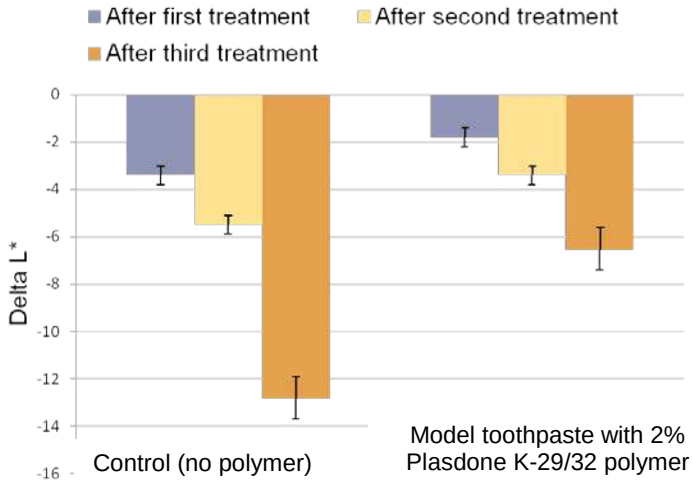


Figure 17
Model toothpaste with Plasdone K-29/32 polymer and stannous fluoride shows greater whiteness compared to control without polymer



In-vitro testing procedures

The testing procedures used are based on work published in the literature[1,2]. The methods are described here.

Outline of test procedure for evaluating in-vitro stain removal from toothpaste

1. Coat supported HAP disks with 1% mucin supernatant (overnight at 37°C)
2. Stain disks with concentrated tea (shake 1 hour at 37°C) and rinse three times
3. Identify each disk and air-dry overnight
4. Measure color of each disk by spectrophotometer and record color before brushing

5. Brush disks with diluted toothpaste on Sabri V-8 Cross Brushing machine (Sabri Dental Enterprises, Inc., Downers Grove, IL, USA)
6. Measure color by spectrophotometer and record color after brushing
7. Calculate E-value (ΔE), the color difference before and after brushing, using the following equation based on CIE L*a*b* color space:

$$\Delta E = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2}$$

Note: The subscripts refer to color before brushing as 1 and color after brushing is 2

Outline of test procedure for evaluating stain removal from mouth rinses

1. Measure color of HAP disks using spectrophotometer and record color before staining
2. Coat supported HAP disks with 1% mucin supernatant (overnight at 37°C).
3. Stain disks with concentrated tea, wine or coffee (shake 1 hour at 37°C) and rinse three times in a large excess of de-ionized water (about 2 liters)
4. Identify each disk and air-dry overnight
5. Measure color of each disk by spectrophotometer and record color before rinsing
6. Incubate in mouth rinse (5 and 10 minutes) then rinse 3 times in large excess of deionized water
7. Measure color by spectrophotometer and record color after rinsing
8. Calculate percent stain removed, the amount of stain removed by the treatment divided by the amount of stain placed on the disk, using the following equation based on CIE L*a*b* color space:

$$100 \times \left(\frac{\sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2}}{\sqrt{(L_3 - L_1)^2 + (a_3 - a_1)^2 + (b_3 - b_1)^2}} \right)$$

Note: The subscripts refer to color before rinsing as 1; color after rinsing is 2 and color before staining is 3

Product Safety

Read and understand the Safety Data Sheet (SDS) before using this product.

References

1. G.K. Stookey, T.A. Burkhard, and B.R. Schemehorn, J. of Dental Research, 61(11) 1236-1239 (1982).
2. J.J. Hefferren, J. of Dental Research, 55 (4) 563-573 (1976).
3. Hunter-Rinderle, et.al., "Evaluation of Cetylpyridinium Chloride-Containing Mouthwashes Using In-Vitro Disk Retention and In-vivo Plaque Glycolysis Methods," J. of Clinical Dentistry, VIII. No.4
4. J. Witt; M. Kaminski; R. Gibb; J. Dunavent; A. Hamilton and J. Coggan; "Relationship Between a CPC Bioavailability Assay and Clinical Performance," presented at 85th General Session of the IADR, Mar. 21-24, 2007.