

# ACNE GEL FOR GREEN EAR SYNDROME? A STUDY ON COPPER CORROSION STAIN REMOVAL FROM POLY (VINYL CHLORIDE)

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The Barbie™ head on the right has extreme "green ear syndrome" from wearing metal earrings. Below, UVC induced illumination displays the area and penetration of the stain

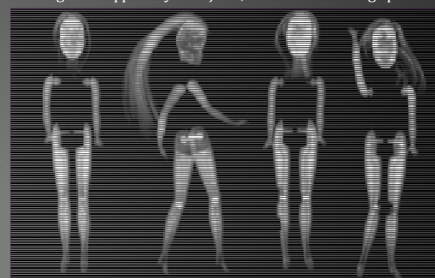


The removal of copper corrosion stains within plasticized poly(vinyl chloride) is of concern to both conservators and collectors of popular vinyl dolls such as Barbie™ and Dawn™. Where the conservation field is hesitant to perform intervention treatments on plastics, public collectors are actively trying treatment methods that employ acne topical gels. Two gels, one with salicylic acid and the other with benzoyl peroxide, were tested according to these amateur methods to determine their ability to remove corrosion stains. The results were observed using normal and fluorescence induced illumination, and X-ray fluorescence spectroscopy (XRF).

Four stained samples were taken from both Barbie™ and Dawn™ dolls along with an additional fifth control sample. Each sample was weighed before and after treatment. Two of each were tested with Neutrogena containing 2% salicylic acid and the other two Clearasil with 10% benzyl peroxide. In addition, one of the pair was placed in sunlight with the gel, per suggested public methods. The gel was applied to half the sample, set over night and then rinsed with de-ionized water. This progressed over 20 days, after which all samples were soaked in de-ionized water for 24 hours.



Dawn™ dolls with green staining at the knees. The dolls have articulated legs with copper alloy metal joints, seen below in x-radiograph.



Sample	Method	%Weight Change
B1	Stained, Salicylic acid, sun	+0.76
B2	Stained, Salicylic acid	+0.65
B3	Stained, Benzyl Peroxide, sun	-1.21
B4	Stained, Benzyl Peroxide	-1.21
D1	Stained, Salicylic acid, sun	+0.49
D2	Stained, Salicylic acid	+0.77
D3	Stained, Benzyl Peroxide, sun	-1.67
D4	Stained, Benzyl Peroxide	-1.47

Table 1: Sample identification, method of treatment and % weight changes before and after test are presented. The salicylic acid had some gain, possibly due to residue left on the surface. The benzoyl peroxide showed an overall decrease in weight indicating loss of material (B = Barbie, D = Dawn).



B1, salicylic acid, before and after



B4, benzyl peroxide, before and after

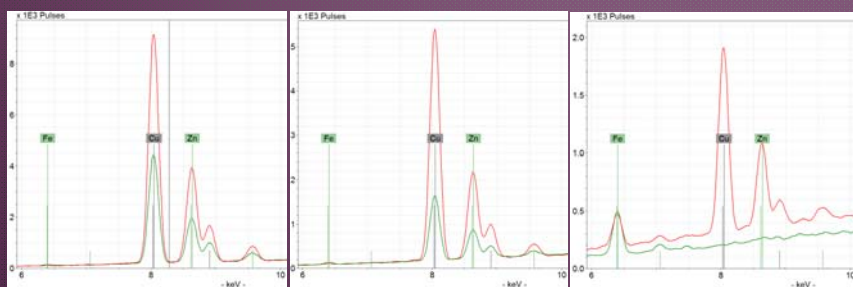


D2 and D3, UVC induced fluorescence, before and after



D4, benzyl peroxide before and after

Salicylic acid treated samples displayed nominal visible difference in normal illumination (top left). The benzoyl peroxide samples had diminished stains, but also loss in material color, a result noted in amateur use and common from bleaching agents (top and bottom right). Sample D4 demonstrates a change in stain color. In UVA-induced illumination the samples had minor fluorescence, while in UVC, the salicylic acid treatment had significant fluorescence, most likely due to dyes present in the acne gel (bottom left).



Comparison of spectra for before and after samples. On left, B1 before (red) and after (green). Middle, D1 before (red) and after (green). On right, D1 swab and salicylic acid control.

The spectra obtained after treatment for both the Barbie and Dawn samples (left) display diminished Cu and Zn peaks, and the Dawn samples also have a reduction in Ca. The swab retained from the D1 sample Day 1 treatment was analyzed and found to contain Cu and Zn. To exclude contaminants, comparison spectra were obtained from a cotton swab, swab with salicylic acid, and swab with benzoyl peroxide and found to not contain Cu or Zn.

	Depth of Cu in PVC		
	Before $\mu\text{m}$	After $\mu\text{m}$	Change $\mu\text{m}$
B1 (SA)	13.7	87.0	73.3
B2 (SA)	13.1	101.6	88.5
B3 (BP)	14.4	53.4	38.9
B4 (BP)	7.3	76.2	69.0
D1 (SA)	3.1	154.9	151.8
D2 (SA)	0.3	137.1	136.8
D3 (BP)	3.5	85.5	82.0
D4 (BP)	0	75.9	75.9

To determine the depth of extracted copper, attenuation calculations were made for copper x-ray photons travelling through PVC. Since the copper is not evenly dispersed throughout the PVC, a theoretical starting point using spectra with the best  $\alpha/\beta$  ratio of K lines was used (D4) and the rest normalized accordingly. The data was collected from area-under-peak for the copper K-lines, and the calculations determined in microns. The change in  $\mu\text{m}$  represents the increased distance copper traveled and thus removal from the PVC. The salicylic tests show the greatest extraction of copper, and thus stain.

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Further analysis will be done using a scanning electron microscopy (SEM) and mapping the elemental copper and its migration within the samples. Artificial aging will help predict the long-term effects on the PVC samples, such as crazing of the surface, cross-linking and yellowing. Gas Chromatography-Mass Spectroscopy (GC-MS) be employed on the swabs saved from Day 1 and Day 4 to determine whether plasticizers were leached from the PVC during treatment.

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