CHROME CONTENT IN BLEACHES AND DETERGENTS
Its Relationship to Hand Dermatitis in Women

Antonio García-Pérez, Agustín Martín-Pascual and Antonio Sánchez-Misiego

From the Departments of Dermatology and Analytical Chemistry, University of Salamanca, Salamanca, Spain

Abstract. From 1967 to 1972 the frequency of eczemas in women with a positive chrome patch-test has decreased strikingly in Salamanca, in comparison with the 1963-66 period. In a 1963 study it was found that 7 out of 9 brand bleaches and 1 out of 3 liquid detergents in domestic use, selected from those most commonly used in this area, contained chromate. In 1972 only 2 out of 9 bleaches were found to contain it. The chromate was not present as impurities, but rather as a component of the product, being added during the manufacturing process in the form of potassium bichromate. Bleaches and liquid detergents containing chromate have been one of the most frequent causes of "housewife's dermatitis" in the Salamanca area.

In 1939 Rabau & Ukraincky (11) observed that eczema of the hands produced by the handling of bleaches could be correlated to their potassium bichromate content. This observation provoked very little response in scientific literature at that time.

In 1961 one of us (A. G.-P.) (6), while working in the Department of Dermatology headed by Prof. Orbaneja in Madrid, studied various cases of hand dermatitis in housewives, produced by the potassium bichromate present in bleaches. Since 1962 we have shown that the way in which this type of eczema arose was very common in Salamanca.

A study carried out in 1963 (4, 5) revealed that many of the bleaches and liquid detergents then in use contained a high proportion of chromate, which was not present as impurities per se, but as bichromate added to the product during the manufacturing process.

In 1972, a decade after our original reports, it was thought that it would be of interest to review the situation, comparing current results with those obtained in 1963 and trying to correlate them with some data compiled from our clinical experience with eczema in women.

MATERIALS AND METHODS
1. The chromate content of some of the bleaches and liquid detergents most frequently used in our area was rechecked in 1972. The study included: (a) Determination of chromate concentration in product samples by means of spectrophotometry using diphenylcarbazide, and, (b) direct inspection of the manufacturing process whenever possible.

The work methods employed did not differ from those used in 1963. Therefore, comparison of current results with those obtained previously did not present any difficulties.

2. In order to check if the differing amounts of chromate in bleaches in the years 1963 and 1972 had a clinical repercussion, the entire file on eczemas, totaling 1,128 case histories in the last 10 years, was reviewed. All cases had undergone a standard series of patch tests, which always included 0.5% potassium bichromate. The following data were selected from these cases:

(a) Frequency of positive chrome patch-test in women with eczema of any type and location, yearly from 1963 to 1972.

(b) Yearly incidence of new cases of hand eczema in housewives or women doing domestic work only, and their frequency of positive chrome patch-test during the same period.

ANALYTICAL DATA

1. The studies carried out in 1963 (4, 5) on 9 brands of bleaches and 3 detergents for household use demonstrated the presence of chromate.
in 7 of the bleaches, and in one of the detergents. The summary of our results is as follows:

It was shown that 5 bleach samples had small amounts (0.1–0.3%) of potassium bichromate added during the manufacturing process (chromium equivalent between 35 and 106 parts per million²).

In 4 other samples of bleach, analytical determinations of chromate by the diphenylcarbazide method were necessary because a direct inspection of the manufacturing process was not possible. Two of them contained 28 ppm of chromium; the other two gave a negative result.

In one liquid detergent, both steps were carried out (direct inspection plus analysis). It was found that during the manufacturing process, between 0.2 and 0.3% potassium bichromate was added; spectrophotometric analysis revealed 76 ppm. The other two detergents did not contain chromate.

2. This study was repeated in January, 1972, on the 9 leading brands of bleach used in this area, as well as the detergent which, in 1963, had been found to contain chromate and which is still widely used in Spain. The chromate tests were carried out using the same techniques as in 1963 (spectrophotometry with diphenylcarbazide). In the case of 4 of the bleaches and detergents it was possible to observe the manufacturing process directly.

In the analytical test, only 2 of the bleaches were found to contain chromate in the proportion of 20 ppm. It was found that about 100–200 g of potassium dichromate was added to 1 700–2 000 l of the product (equivalent to potassium dichromate solution of 0.05–0.12 per thousand). The remaining 7 samples gave negative results or contained less than 1.2 ppm of chromium. The actual manufacture of 2 of these bleaches was observed, verifying that dichromate had not been added. At present, no dichromate is added to the liquid detergent in question and analytical tests have demonstrated that it is dichromate-free.

### CLINICAL DATA

Table I and Fig. 1 summarize the incidence (%) of positive chrome patch-tests in eczema (regard-

Fig. 1. Positive patch-test to chrome in women with eczema of any type and location.
Table II. Incidence of eczema on the hands of housewives or domestic workers

<table>
<thead>
<tr>
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<th>1963-66</th>
<th>1967-72</th>
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<tbody>
<tr>
<td>Total out-patients examined</td>
<td>156</td>
<td>178</td>
</tr>
<tr>
<td>Average new cases/year</td>
<td>39</td>
<td>29.6</td>
</tr>
<tr>
<td>Cases positive to Cr (%)</td>
<td>47</td>
<td>5</td>
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</tbody>
</table>

Incidence of eczema on the hands of housewives or domestic workers between 1963 and 1972. Table II and Fig. 2 present the incidence of eczema on the hands in housewives or domestic workers, as well as the number and percentage which demonstrated a positive chrome patch-test every year, in the same periods.

Fig. 3 shows the percentage of positive chrome patch-tests in any type of eczema in men and women. The study has been divided into two periods: 1963–66 and 1967–72.

**DISCUSSION**

**Analytical data**

Rabau & Ukraincyk (11) found an average ratio of 0.07 per thousand of potassium bichromate (equivalent to 25 ppm of chromium) in several samples of Javel's solution. The chromate was not present as an impurity but as a component added during the manufacturing process. In our 1963 study (4) it was found that 7/9 of the bleaches and 1/3 of the liquid detergents used in Salamanca contained potassium bichromate, added during production, in proportions varying from 0.1 to 0.3 per thousand (equivalent to more than 25 ppm of chromium). At our present repeat study, it has been found that bichromate is added to 2/9 bleaches in amounts of 0.05 to 0.12 per thousand. Analysis has also shown that only these two bleaches contain chromium equivalent to 20 ppm.

Bleach or Javel water is a solution of sodium or potassium hypochlorite, usually obtained from a mixture of solutions of calcium hypochlorite and sodium or potassium carbonate. The addition of bichromate has three objectives: (a) to stabilize the mixture, avoiding the transformation of the hypochlorite into chloride or chlorate; (b) to clarify the final product, oxidizing and removing impurities; (c) to colour the solution. The majority of manufacturers claim to use it for the latter purpose. A 1947 Industrial Chemistry Formulary, still commonly used, states: "The addition of bichromate serves to give the bleach an amber color which improves its commercial presentation" (9). The problem is distinct from that studied by other investigators, who detect chromium and/or nickel in detergents in proportions generally much lower than those found in bleaches (7, 8, 10). Their presence is interpreted as being due to impurities in the raw materials (7, 8), or as being released from the industrial stainless steel installations in which these detergents are prepared (10).

**Clinical data**

The clinical data set out in Table I and Fig. 2 show that the incidence of positive chrome patch-tests in women with eczema, decreases markedly from 1963 to 1972. The curve makes a very prominent dip from 1967. In the period 1963–66 the average incidence of positive tests is ex-
tremely high (22%), much more so than the average of Fregert et al. (3), reporting collective results from 8 European clinics (3.6%). Our mean for 1967–72, on the other hand is 1.6%. However, in male eczemas of any type, we do not find any difference in frequency in the patch-test during the same periods (1963–66: 25.7%; 1967–72: 23.3%) (see Fig. 3 and Table III).

A similar picture can be seen in Table III. The frequency of positive chromium in hand eczema of any type, found in housewives or women doing domestic work only, is in our series: 30.1% during the period 1963–66. This is much higher than the 3% found by Calnan et al. in 1970 among 1,000 patients doing domestic work only (1). However, our data are comparable to Feuerman's (2) in Israel, who find 47/50 chrome positive cases in “housewife's dermatitis” and 51 out of 150 cases in contact dermatitis in women with hand eczemas.

The decrease in the frequency of chrome positive patch-test in our patients since 1967 can be explained by the fact since then, bleaches start being replaced by other detergents. The few brands of bleaches that continue in use today are, for the most part, not produced by the small local industry, but by national-scale manufacturers who do not add dichromate. Similarly, a very popular national liquid detergent which contained bichromate in 1963, currently does not do so.

Finally, we believe that the bichromate contained in bleaches and liquid detergents has played a fundamental causative role in hand dermatitis among housewives in our area. However, it is quite likely that the problem differs in each country.

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A. Garcia-Perez, M.D.
Department of Dermatology
Faculty of Medicine
Fonseca, 2
Salamanca
Spain