Acta Dermatovener (Stockholm) 52: 221–224, 1972

SENSITIZATION TO CHROMIUM AND COBALT IN PROCESSING OF SULPHATE PULP

S. Fregert, B. Gruvberger and A. Heijer

From the Department of Dermatology, University of Lund and University of Umeå, Sweden

Abstract. Two men working in the recovery process in a sulphate pulp factory had developed eczema on their hands and faces. Both gave positive reactions to chromium and one also to cobalt at routine patch testing. This finding initiated examination of samples from different stages. In samples from the "recovery process" both tri- and hexa-valent chromium as well as cobalt were found. The chromium is oxidized to hexavalent form in the lime kiln. The chromium and cobalt seem to be added to the process as Na_2SO_4, CaO and $CaCO_3$, used as "make-up chemicals". The content of chromium varied considerably. The highest content, 3 300 μg Cr^6/g, was found in a special form of Na_2SO_4, "chrome-cake", obtained as a by-product of production of chromic acid. Such Na_2SO_4 must not be used in pulp factories. Chromium was also found in Na_2SO_4 of high technical and of *pro analysi* quality. It is pointed out that this substance also occurs in detergents and is used in the determination of "adsorbed" chromate in cement.

During the last two years two patients with contact allergy to chromium and cobalt, working in sulphate pulp factories have been examined. To trace the chromium and cobalt sources, several samples from different stages of the sulphate process in one factory and the chemicals used have been analysed.

MATERIAL AND METHODS

The sulphate pulp process (4)

The kraft process. Wood chips (*a*) are cooked with alkaline liquor in digesters (*b*). The "cooking liquor" (*c*) containing sodium hydroxide and sodium sulphide dissolve the cementing material of the wood. "Sulphate turpentine" (*d*) is condensed from gases released. The liberated fibres, largely cellulose, and spent chemicals are separated on washers (*e*). The fibres are at this point ready for papermaking (*f*), eventually after bleaching.

The recovery process. The "weak black liquor" (*g*) from the washers is concentrated in an evaporator (*h*). A semi-solid crude "sulphate soap" (*i*) can be skimmed from the top of the evaporator tank. This soap can be neutralized with acid, producing tall oil. The "strong black liquor" (*j*) is sprayed into a recovery furnace (*k*). The organic material is burned and the inorganic chemicals are then converted into the "soda solids" (Na_2CO_3 and Na_2S). Some soda gets lost in the washing operation and is replaced by addition of crude sodium sulphate or "Glauber's salt" (I). This is reduced during the burning process to sodium sulphide (Na_2S). The soda solids are melted in the furnace and discharged into a tank of water forming the "green liquor" (*l*). This contains sodium sulphide, sodium carbonate, carbon and iron sulphides (green). In the causticizer (*m*) the sodium carbonate is converted into sodium hydroxide and calcium carbonate by the addition of lime (II) and heating. The causticized liquor is separated in a clarifier (*n*) in a slurry of calcium carbonate (*o*) and "white liquor" (*p*). Together with added limestone (III) the calcium carbonate is converted into quick lime at 900°C in a rotary lime kiln (*q*) of the same kind as cement kilns and becomes available for causticizing (*m*). The "white liquor" (*p*) is used as cooking liquor (*b*). The process is automated, but because of leakage the vicinity of the tubes, kilns and vessels is contaminated by chemicals.

Determination of chromium and cobalt

Chromium and cobalt content was determined in an Atomic Absorption Spectrophotometer (Perkin-Elmer 303) at 3 577 respectively 2 407 Å.

For determination of *total chromium and cobalt* the weak black liquor, green liquor and white liquor were aspirated directly into the Spectrophotometer flame without any preparation. The strong black liquor, a thick mass, was first diluted with water. The samples of CaO and $CaCO_3$ from the kiln as well as the technical and *pro analysi* samples were dissolved in 3 M HCl before total chromium and cobalt determination.

These substances were shaken with water for 15 min before determination of the *soluble chromium* content.

Sodium sulphate, Na_2SO_4, was dissolved in water. This substance produces a high "salt effect" in the Atomic Absorption Spectrophotometer, thus the absorption was also measured at 3 528 Å. The *hexavalent chromium* (Cr^6) was chelated by ammonium pyrrolidine-di-thiocarbamate at pH 8.0. The chelate was extracted from the water solution by methyl-*iso*-buthylketon.

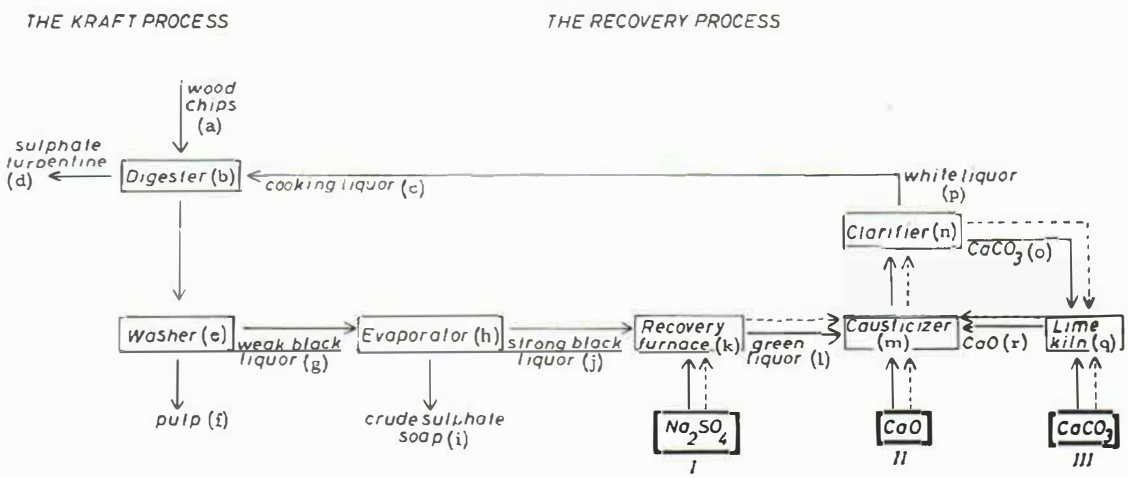

Fig. 1. Flow diagram for the sulphate process.

The *trivalent chromium* (Cr^3) was calculated as the difference between the values of the total and the hexavalent chromium.

Samples from different stages of the sulphate pulp process and of the substances added to the process are given in Table I. All samples from the process except the green liquor were obtained on an occasion when Na_2SO_4 containing 572 μg Cr/g was used. The green liquor was obtained later when Na_2SO_4 contained 5 μg Cr/g. Six other technical and six *pro analysi* samples of Na_2SO_4 from different producers were analysed. Two technical and one *pro analysi* sample of CaO and two technical ones of $CaCO_3$ were analysed.

Case 1

A man, aged 50 (Dept. Derm., Umeå), had been working in the recovery process in a sulphate pulp factory for one year. He developed eczema on his hands and ankles and also in the face. When patch tested he showed positive reaction to chromium but negative to cobalt and nickel. He tried to continue the same work for one year. During holidays and sick-leave periods he recovered but worsened immediately on returning to work. For this reason he changed his occupation. Unfortunately he then came in contact with another source of chromium, namely zinc galvanized sheets (2). Hence, not until he had changed his work once more, was he clear of eczema.

Case 2

A man, aged 66 (Dept. Derm., Umeå), had been working for 50 years in a sulphate pulp factory and for the last 15 years in the recovery process. He had for the last 3 years had eczema on his hands and arms and periodically in the face. He had recovered during holidays and sick-leave periods but had immediately worsened on returning to work. Patch testing showed positive reactions to chromium and cobalt but negative to nickel. After 2 months' sick-leave his eczema cleared up completely and he then retired with an annuity.

Table I. *Chromium and cobalt in samples from different stages of the sulphate pulp process and in chemicals used in the recovery process*

Samples from the process		μg Cr^3/g	μg Cr^6/g	μg Co/g	pH
Weak black liquor (g)[a]		0.1[b]	0.0	0.0	12.6
Strong black liquor (j)		2.2	0.0	0.0	10.0
Green liquor (l)[c]		0.4[b]	0.0	0.0	12.6
White liquor (p)		0.1[b]	0.0	0.0	12.4
$CaCO_3$ from clarifier (0)		168.0	0.0	0.0	12.0
CaO from lime kiln (r)		0.0	248.0	9.0	12.4
Chemicals					
Na_2SO_4[d]	Technical (I)	182.0	390.0	0.0	
Na_2SO_4[d]	Technical	1.3	3.7	0.0	
Na_2SO_4[e]	Technical	0.0	3 300.0	0.0	
Na_2SO_4[e]	Technical	1.3	2.8	0.0	
Na_2SO_4[e]	Technical	1.4	0.0	0.0	
Na_2SO_4[e]	Technical	0.6	0.0	0.0	
Na_2SO_4[e]	Technical	1.2	0.0	0.0	
Na_2SO_4[e]	Technical	6.7	0.0	0.0	
Na_2SO_4	Pro analysi	0.7	0.2	0.0	
Na_2SO_4	Pro analysi	1.0	0.3	0.0	
Na_2SO_4	Pro analysi	0.3	0.0	0.0	
Na_2SO_4	Pro analysi	0.7	0.0	0.0	
Na_2SO_4	Pro analysi	0.4	0.0	0.0	
Na_2SO_4	Pro analysi	0.3	0.0	0.0	
CaO	Technical (II)	0.8	6.8	7.0	
CaO	Technical	0.0	23.0	0.0	
CaO	Pro analysi	0.0	0.0	0.0	
$CaCO_3$	Technical (III)	1.2	0.0	0.2	
$CaCO_3$	Technical	0.0	0.0	0.5	

[a] Figures in ( ): see the Flow Diagram.
[b] μg/ml.
[c] Sample taken when Na_2SO_4 (I) used contained 5.0 μg Cr/g.
[d] Cr and Co values are calculated on waterless Na_2SO_4.
[e] Chrome cake.

RESULTS

The analytical results of the chromium and cobalt content in samples from different stages of the sulphate pulp process and in chemicals used are given in Table I.

DISCUSSION

The two patients who had developed eczema after having worked for 1 and 12 years respectively with the recovery process, showed positive reactions to chromium at routine patch testing. Furthermore, one of them reacted to cobalt. The presence of chromium and cobalt in the working process was suspected.

In a preliminary investigation chromium was found in the slurry of calcium carbonate (*o*) from the clarifier. This initiated a close study of chromium and cobalt content in samples from different stages of the recovery process and of chemicals added.

In the process about 5% of the chemicals are lost and Na_2SO_4 (I), CaO (II) and $CaCO_3$ (III) are the "make-up chemicals". In all the 14 samples of Na_2SO_4, trivalent chromium (Cr^3) was found and in 6 of them also hexavalent chromium (Cr^6). A very high content of Cr^6 was found in two samples. One of these, containing as much as 390 μg Cr^6/g, was used in the process when the samples from the different stages were obtained, all except the green liquor (*l*). The two samples containing 390 and 3 300 μg Cr^6/g were yellow. This kind of Na_2SO_4 is obtained as a side-product from the processing of chromic acid and is called chrome cake. It is noteworthy that all six samples of Na_2SO_4 *pro analysi* also contained Cr^3 and two of them Cr^6. Some authors have reported that detergents which usually contain Na_2SO_4 are contaminated by chromium, but others have denied the presence of this substance (3). The small amounts and the variation of the chromium content may explain the different results.

Na_2SO_4 is used in the process of determining the amount of "adsorbed" chromate in cement (1). In such an investigation it is therefore necessary to determine the chromium content in the actual Na_2SO_4. This substance is also used in manufacture of glass. The results show that chromium is continuously brought to the pulp process mainly by Na_2SO_4 but also by CaO and $CaCO_3$. The amount can, however, vary considerably. Cobalt may also be brought into the process; here by CaO and $CaCO_3$. Chromium in samples from the process itself was mainly found in CaO (*o*) from the lime kiln (*n*) and in $CaCO_3$ (*r*) from the clarifier (*q*). The $CaCO_3$ (*o*) contains only trivalent chromium, since the environment, with the sulphides present, is reducing. The only trivalent chromium is then oxidized to hexavalent on heating at 900°C in the alkaline lime kiln (*q*).

The white liquor (*p*) which goes back to the kraft process contained very little chromium and no cobalt. Thus the main chromium and cobalt seem to "circulate" within the recovery process. The green liquor (*l*) may contain more chromium than the present investigation shows on occasions when Na_2SO_4 with high chromium content is used.

Workers in the recovery process can easily be exposed to chromium and cobalt containing material. The region of the lime kiln, in particular, is highly contaminated by dust (CaO). Furthermore cleaning and repair of kilns, vessels, tubes, filters, washers, pumps as well as sample-taking for technical control imply risk of contamination. The skin can also be damaged by the alkalis. The sensitization of the two workers is therefore easily understood. According to the managers of the actual pulp factories several other workers have earlier developed hand eczema and for this reason left the work. They do not seem to have been patch tested.

The two workers in question had been on sick-leave several times due to their hand and face dermatitis but had never been patch tested on these occasions. By patch testing the two workers and by analysing samples from the working place it has been possible to explain the cause of the allergic contact dermatitis. One of the patients (case 1) has come in contact with two different, until recently unobserved sources of chromium.

As there is a potential risk of chromium and cobalt sensitization, as well as skin damage by alkali, preventive measures must be considered important. It is necessary to inform employers and employees about the risk. Sodium sulphate with large contents of chromate must not be used. As many stages of the work as possible, should be automated, for example the supply of make-up chemicals.

During special working stages with a high risk

of contact, protective clothing such as plastic gloves and rubber boots should be used. When the kilns are cleaned special protective clothes should be worn. The dusting of the premises should be reduced. Personal hygiene is here, as in most kinds of work, of great importance.

ACKNOWLEDGEMENT

This investigation was supported by grants from Riksförbundet mot allergi.

Addendum

Recently we have examined a third case, a man aged 61 (Dept. Derm., Uddevalla). He had been working in a sulphate paper pulp factory for 40 years though not within the recovery process.

During the last 10 years he had had daily contact with Glauber's salt (I), chalk (II) and sulphate turpentine (d).

For the last 4 years he has had hand dermatitis continuously and periodically also on the face, arms, and legs. The dermatitis has healed partly during sick-leave periods and holidays.

Four years ago he was tested and found positive to chromium, but negative to turpentine. He was not tested with cobalt on this occasion. At that time it was not known that the chemicals at his place of work could contain chromium.

Recently he was re-tested and was found to be positive to turpentine and also to cobalt. He intends to retire because of the chronic course of the dermatitis.

REFERENCES

1. Brun, R.: Contribution à l'étude des chromates du ciment. Nouvelle technique pour le test épicutané au ciment. Dermatologica *129*: 79, 1964.
2. Fregert, S., Gruvberger, B. & Heijer, A.: Chromium dermatitis from galvanized sheets. Berufsdermatosen *18*: 254, 1970.
3. Hjorth, N. & Fregert, S.: Contact Dermatitis. *In* Textbook of Dermatology (ed. A. J. Rook, D. S. Wilkinson & F. J. G. Ebling), 1st ed. Blackwell, Oxford, 1968.
4. Sawyer, F. G., Holzer, W. F. & McGlothlin, L. D.: Kraft Pulp Production. Ind Eng Chem *42*: 756, 1950.

Received September 10, 1971

Sigfrid Fregert, M.D.
Section of Occupational Dermatology
University Hospital
S-221 85 Lund
Sweden