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Skin contact with gold and gold alloys

W. S. Rapson

International Gold Corporation Limited, The Corner House, 63 Fox Street, 2001 Johannesburg, South Africa

3 types of reaction to gold merit discussion. First, there is the effect known as black dermographism, in which stroking with certain metals immediately produces well-defined black lines on the skin. Some gold alloys are amongst such metals. The evidence indicates that the effect is the result of impregnation of the skin with black metallic particles generated by mechanical abrasion of the metal by contaminants of the skin. There is no positive and unequivocal evidence of the ability of metals to mark uncontaminated skin so rapidly that it is possible to write upon it.

Secondly there are the 2 related phenomena of the wear of gold jewellery, and the susceptibility to certain individuals to blackening of the skin where it is in contact with such jewellery. The occurrence of smudge, as it is often called, is not very common, but is brought to the attention of most jewellers from time to time. In extreme cases it may make it embarrassing for the person concerned to wear metallic jewellery. It would appear as if gold smudge also results mainly from mechanical abrasion of jewellery, though this may be aided and/or supplemented in some instances by corrosion of gold or gold alloy induced by certain components of the sweat.

Finally, there is the question of true allergic responses to contact of the skin with gold and its alloys. Judging from the very few cases which have been recorded, such responses are extremely rare. Some recent observations on the reactions of metallic gold with amino acids and of reaction to contact of the skin with gold on the part of rheumatoid arthritis patients undergoing gold therapy, are, however, relevant in this connection.

Key words: Gold – gold alloys – jewellery – black dermographism – wear – tarnishing – corrosion – skin – allergic reactions.

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Black Dermtographism of Gold and Gold Alloys

Although there is a reference by Bechet, in discussion of a paper of Urbach & Pillsbury (1), to a monograph in French on dermographism, published some 60 years previously, no details are given of this work and it has not proved possible to identify it. It was stated, however, that the monograph contained a chapter on black dermographism which included reference to the part played by this phenomenon in demonology, black magic and witchcraft in the middle ages.

It is apparent, therefore, that the fact that it is possible to write on the skins of certain individuals with certain metals has long been known.

The earliest scientific description of the effect in the English language which has been identified, is contained in a note from King's College Hospital in London in 1879 by Ferrier (2) who followed up an observation by a colleague, Wood, on a patient with paralysis of the cervical sympathetic on the left side and complete paraplegia from the mid-thoracic region downwards. Wood had noted that a silver probe made dark pencil marks on the paralysed parts, whereas it produced only red marks of vascular dilatation on the unparalysed parts of the patient. Ferrier found, *inter*

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etel (7), Krantz (8), Hosp (9), Bork (10), Dietel (11), Joch (12), Riehl (13), Goldschlag (14) and Koga (15) concluded from their studies that the mechanism was indeed mechanical and associated with contamination of the skin with mineral particles.

Aspects of the work of these and subsequent investigators which are relevant in the context of the present review are described in more detail below.

Metals Which Produce Black Dermographism

A list (1) of metals producing black dermographism includes not only gold 'less fine than 18 carat' but also silver, copper, aluminium, nickel, zinc, tin, lead and brass. This list could be expanded. A parallel list of metals which do not produce the effect includes gold 'finer than 18 carat', along with iron and platinum.

Unfortunately, in regard to the gold alloys tested, no details of compositions or metallurgical histories are given. The data are therefore, incomplete and possibly unreliable. This aspect is discussed in detail later in this review.

Contaminants of the Skin Which Promote Black Dermographism

Following on the original work of Emdin & Kusmenko (3) and Emdin (16), information accumulated rapidly concerning the rôle of contaminants in promoting the marking of skin by metals. Thus Breitmann (4a, b) found that black dermographism occurred not only with women who used face or body powders, but also with factory and other workers who worked in dusty environments and who never used such powders. Thus Markow et al. (17) reported a high incidence of black dermographism amongst persons engaged in such occupations as cement mixing, stucco work, etc. A number of workers (7) and (9) especially found contamination with zinc oxide particularly effective.

The most exhaustive study of contaminants, however, was that of Urbach & Pillsbury (1) who studied the effects of a wide range of powdered materials under standardized con-

alia, that the edge of a bright sovereign, which would almost certainly have been of the standard 22 carat alloy, produced dark marks similar to those made by silver, though less readily and less distinctly. He also observed black marking with copper, lead, zinc and magnesium but only red vascular dilatation markings with iron, platinum and arsenic.

During the course of his experiment, he burnished one of the metals he was using with wash-leather, and noting that this was blackened in the process, he tested all the metals on wash-leather and found them to behave towards it as they did towards the skin of the paralysed parts of his patient. He finally concluded that the blackening was the result of metal abrasion, which produced black particles of metal, that it was an attribute to a greater or lesser extent of all healthy skin, but that under certain conditions, especially of oedema, the effect was intensified.

The next identified publication was from Russia, where Emdin in 1925, also came across black dermographism by chance and followed it up in collaboration with his colleague Kusmenko at the State University at Rostow-on-Don. Together, these investigators studied some 800 patients in neighbouring clinics, hospitals and sanatoria. They concluded (3) that if skin was dry, oiled by very thorough rubbing in of vaseline and powder applied, it was possible to make black marks upon it with a number of metals. In the light of this and the immediate nature of the blackening reaction, they dismissed the possibility of a chemical mechanism for black dermographism and concluded, as had Ferrier previously, that the effect was purely a mechanical one, with powder contamination of the skin playing a crucial rôle.

This paper stimulated studies of further aspects of the phenomenon by investigators in Russia and Germany. A few of these and in particular, Breitmenn (4a, b), Jurjew (5) and Russinow and Sutorochin (6) postulated chemical mechanisms, but these enjoyed little support. The majority including Hauck & Di-

ditions, and included in their investigations a study of 20 brands of face powder. All brands made writing on skin possible and of their constituents, titanium dioxide and calcium carbonate were particularly effective in this respect. The authors were unable to find any correlation, however, between occurrence of the effect and the relative hardnesses of the metal and powder combinations used in the tests.

Effects of Skin Properties

Non-fatty and dry skins were found to mark much more easily than fatty and/or moist skins. This was interpreted as due to the lubricating effects of fat and moisture. It explained, for example, why the skin between the breasts or in the middle of the back was marked more easily than on the forehead (7). The latter was found to have a higher fat content (9). The horny layer of the skin was also found to play a rôle. Thus it has been found that it is easier to write on the thick keratin of the palm of the hand than it is to write on the inner side of the upper arm.

Effects of Disease, Endocrine Disturbances etc.

A number of workers have studied the incidence of black dermographism on patients and others suffering from various disturbances of health.

An early suggestion (3) that susceptibility to writing on the skin with metals was especially common amongst patients suffering from hysteria was later found untenable and abandoned (16). The most comprehensive studies were probably those of Hosp (9) and Hauck & Dietel (7), who studied such susceptibility in a wide range of subjects suffering from various venereal and skin diseases, from disturbances of endocrine function, from malfunctioning of organs and from a range of miscellaneous conditions. No correlations could be drawn and a particular susceptibility to skin writing amongst patients suffering from skin disease was found attributable to external treatments of these diseases with medicaments containing zinc oxide.

With regard to the effects of endocrine disturbances, the ability to write on the skin was at first thought to be enhanced in patients suffering from thyroid deficiency, but this was never substantiated.

Perhaps of greatest interest, especially in relation to the marking of the skin by jewellery, however, was a claim by Rühl (17a) that the skin of women during the premenstrual period was particularly prone to blackening by jewellery, especially where there was actual rubbing, as opposed to gentle contact, between it and the skin. Rühl's claims were later followed up by a number of investigators including Spier (18), Genzel (19), Albrecht (20), Polemann (21) and Hauck & Dietel (7). In the light of the available information, Rühl's claims were not regarded as convincing by Soltermann (22). Polemann and Spier had attributed blackening of the skin to the formation of sulphides of the metals, generated by their interaction with labile sulphide compounds in the sweat which was seen as being hormonally controlled during the premenstrual period. Both Spier (18) and Genzel (19) had recommended treatment with vitamin C and diuretics in such cases and claimed that this cured the tendency to blackening of the skin by jewellery.

Comfirmation of the Abrasive Mechanism

Microscopic examination of marked skin has been described by many workers, who have recorded the presence on it of specks of black material. In the case of paper impregnated with zinc oxide particles and marked with a gold ring, the particles had a golden gleam.

Of more significance, however, is an electron microscopy study described by Soltermann (22), which yielded confirmation of the presence, in black markings, of relatively large particles of abraded metal.

Wear of Gold Jewellery by Friction with the Skin, and the Smudge Phenomenon

Wear of gold jewellery may be caused in a number of ways; through rubbing against the skin and clothes, through friction between component parts such as the links in chains, and through tarnish and corrosion. In the light of the review of black dermographism above, it will be apparent that the abrasive mechanism established for it must also be operative with respect to wear caused by rubbing against the skin.

There is, however, a very important difference between the conditions under which skin may be marked when it is written upon using gold and gold alloys and the conditions under which jewellery made of the same alloys comes into contact with the skin when it is worn. In writing upon skin there is transient frictional contact between the metal and the skin, whereas in the wearing of gold jewellery, contact between the skin and the jewellery may be prolonged and may vary considerably in nature from gentle contact as in the case of a pendant to close rubbing contact as in the case of a ring, bangle, watch or watch-band.

Moreover, gold jewellery may be worn intermittently and seldom cleaned before use, in which case it may have on it before it is worn, thin films of dried perspiration and adherent dust and – in the case of low caratage items – of the products of tarnishing which may have taken place while it was being stored. There is the possibility in the case of such jewellery that the skin may be marked not necessarily by the metal but by transfer to it of contaminants of the metal. There is also the possibility that where jewellery is tarnished or corroded, this may involve preferential attack on one or more of the jewellery alloy components and may leave the surface of the alloy more susceptible to abrasion.

Such attack normally occurs along intergranular boundaries so that the bonding between the metal grains in the corroded surface is weakened. The effects of abrasion then probably depend upon the extent to which the residual surface grains have been enriched in gold. If they are highly enriched, the predominant effect is likely to be burnishing and consolidation of the surface with little loss of metal. If they are not greatly enriched, which is very likely in a practical situation in which corrosion and wear occur simultaneously, then the effect is likely to be a dislodging of metal grains from the surface and increased metal loss.

Established facts in this whole area of gold jewellery wear and of smudge production are very few and the task of generating them is very difficult. Appropriate attention must be paid not only to the metallurgical histories of the alloys (23) but also to the degree and nature of the contamination of the skin with abrasive powders and to the factors which may promote tarnishing and corrosion.

The following discussion highlights those aspects of the subject which are of significance.

Abrasive Wear Through Friction with the Skin and Dermographism

Our knowledge of black dermographism indicates that wear should be increased and smudge production made more likely where jewellery is worn by persons with dry, non-oily skins and where use is made of face or body powders. Very little powder may be needed, the effects of one application may endure for an appreciable time, and may extend beyond the site of original application. Even if powder is not used, contamination of the skin by abrasive particles may occur as a result of exposure to dusty environments or fabrics. The between-breasts and mid-back positions may cause more wear and show more frequent smudge production than might be expected from the gentle nature of the contacts between jewellery and the skin in these positions, because of the relatively non-oily character of their skin. Both wear of, and marking by, carat gold rings, bangles, watch-cases and watch-bands may be greatly enhanced as a result of handling of or contact with dust or grit generally.

Rubbing of jewellery items by fabrics impregnated with abrasive particles may be a factor in the wear of the alloys involved and may lead to marking of the fabrics.

Effects of Caratage and Metallurgical Histories on Wear of Gold Jewellery

Because of its softness, low strength and great ductility, pure gold is not suitable for jewellery unless this is of massive construction. It scratches easily and might therefore be expected to wear rapidly by abrasion. It is nevertheless not listed among metals which mark skin, even when this has been contaminated by a material such as zinc oxide powder. This appears anomalous, but may be explained in terms of the findings of Heidsiek & Clasing (24). These authors recently described the results of an investigation of the abrasive wear of one 18 carat and two 14 carat gold jewellery alloys by 'microcut', which is a polishing cotton normally used in the preparation of metallurgical microsections and which is lightly impregnated with silicon carbide particles (<15 μm).

The hardness of the alloys was varied by a range of mechanical and thermal pre-treatments and, in the case of one of the 14 carat alloys, by the incorporation of additives (grain refiners). The abrasive wear resistances of the alloys in their different forms were then measured under standardized conditions.

Although the hardness of the one 14 carat alloy could be varied between 120 HV (soft state) and 312 HV (cold worked and annealed state), increase in hardness was not accompanied by increase in wear resistance. Indeed under the test conditions, the abrasive wear resistance in the hardest state was 10% less than that in the soft state. These results indicate that, contrary to what is often presumed, hardness is *not* a suitable indicator of abrasive wear resistance for this alloy. In fact, the highest wear resistance was observed in the case of the alloy in a soft state (155 HV) which was achieved by addition to it of 0.25% of yttrium.

This conclusion was confirmed in the more limited studies of the other 14 carat alloy and of the 18 carat alloy.

These findings are readily understood in terms of the 2 mechanisms for abrasive wear which are generally recognized, namely micro-cutting and micro-ploughing. The amount of material removed, and therefore the wear rate, is high if micro-cutting prevails, since it leads to immediate material loss. In micro-ploughing, however, the surface undergoes mainly deformation without material loss. The higher the ability of a surface to absorb plastic deformation, the higher will be the extent to which micro-ploughing occurs and the higher the wear resistance.

It is tempting to extrapolate from these results and from the tribological conditions employed by Heidsiek & Clasing (24), and to conclude from their findings that the failure of pure gold to mark skin is a consequence of its ease of deformation and therefore a predominance of micro-ploughing over micro-cutting during rubbing by the skin. It is also tempting to conclude that the abrasive wear of gold jewellery by skin and therefore its dermographic effectiveness must be less affected by its caratage, than by its ability to undergo plastic deformation in the state in which it is tested. It would be rash, however, to be in any way dogmatic about conclusions drawn on this basis even though Taylor (25) has demonstrated in practical trials conducted over a period of 1 year that 18 carat gold alloys can be equally as durable as those of 9 carat purity.

The Rôle of Tarnish and Corrosion in the Wear of Gold Jewellery in Coctact with Skin

The literature on the tarnishing of gold alloys used in electrical contacts by exposure to the atmosphere in a wide range of environments is extensive. For the purpose of the present review, perhaps the most important facts which have emerged are first, the tendency for overall resistance to tarnish to increase with gold content of the alloy and, secondly, the important rôle which sulphur compounds can

Table 1. The effect of pH on the solubility of 24 carat gold in 10^{-1}M cysteine, glutathione, penicillamine, alanine and histidine solutions which were analysed after standing in contact with gold for 1 month (after Brown et al. (27))

Amino acid	pH	Gold uptake g/ml	Solution appearance
L-cysteine	1.2	0.3	black precipitate
	7.2	2.0	white/black precipitate
	9.5	22.1	white precipitate
glutathione	1.6	0.6	black precipitate
	7.2	8.0	black precipitate
	9.5	33.1	black precipitate
D-penicillamine	1.6	0.4	black precipitate
	7.2	10.2	black precipitate
	9.5	18.5	black precipitate
L-alanine	1.6	0.2	clear solution
	7.2	0.1	clear solution
	9.5	0.2	clear solution
L-histidine	1.6	1.2	faint black precipitate
	7.2	2.1	faint black precipitate
	9.5	1.8	faint black precipitate

play in the tarnishing, especially of lower gold content alloys. Experience has confirmed that these findings also apply to the carat gold alloys used in jewellery fabrication. Only low caratage alloys tarnish, and then only in more aggressive environments. The work of Treacy & German (26) on the tarnish and corrosion characteristics of dental gold alloys is of interest in this respect and confirms these trends.

The type of tarnishing which is of greatest significance for the wear of gold jewellery and the marking by it of the skin, is that which may be promoted by substances secreted by or derived from the skin. The substances of most immediate interest in this connection are amino acids and in particular the sulphur-containing amino acids. Recent investigations reviewed by the author have suggested that metallic gold in the soil can be rendered soluble and taken up by plants and micro-organisms through reaction with amino acids and, in the case of certain plants, through reaction with cyanide generated from cyanogenetic glycosides, which are secreted into the soil.

In this connection the work of Brown et al. (27) who have recently studied the reactions of gold in the form of foil and as colloidal gold with a range of amino acids, both sulphur-containing and sulphur-free, is very significant. The uptake of gold from the massive form in different solutions is shown in Table 1.

Like Russian investigators before them, whose work is described by Rapson (28), they found that over a long period (1 month), significant amounts of gold were dissolved by solutions of sulphur-containing amino acids such as L-cysteine, glutathione and D-penicillamine, while much smaller amounts were dissolved by sulphur-free amino acids such as L-alanine and L-histidine. Solution took place with the formation of black or white precipitates in some instances and was favoured by raising the pH in the case of the thiol-containing amino acids. The precipitates contained gold and appeared to be gold complexes when white, and largely metallic gold – presumably formed as a result of the decomposition of initially formed but unstable complexes – when they were black. The addition of hydrogen peroxide facilitated the attack on the gold by the sulphur-free amino acids. Hydrogen per-

Table 2. Gold and copper concentrations (g/ml) from 9, 18, 22 ct. gold in histidine and glycine 10^{-1}M) (after Brown et al. (27))

Amino acid	Gold alloy (ct.)	Solution concentration (g/ml) gold (no hydrogen peroxide)	copper (no hydrogen peroxide)	gold (with hydrogen peroxide)	copper (with hydrogen peroxide)
histidine	9	4.7	1.2	11.1	21.8
	18	1.9	1.2	7.1	1.3
	22	1.2	0.6	6.8	0.6
glycine	9	0.6	0.3	4.6	1.0
	18	0.3	0.3	3.6	0.5
	22	0.2	0.3	3.2	0.4

oxide could not be used with the thiol-containing amino acids because of its reaction with them to form disulphides.

As a most interesting extension of their work on gold itself, Brown et al. (27) studied the dissolution of gold and copper from a series of massive gold-copper alloys by L-histidine and glycine in the presence of hydrogen peroxide. The results (Table 2) suggest that the peroxide accelerated the oxidative dissolution of metal and that the higher the copper content of the alloy the more gold and copper were dissolved. This is in tune with the known ease of solution of copper in amino acids. The enhanced solubility of the gold was interpreted as possibly due to the increased area exposed by the dissolving copper. These limited experiments are sufficient to demonstrate that a range of amino acid solutions is capable of dissolving at least gold and copper from carat gold alloys and therefore from jewellery made from such alloys. Moreover, dissolution was often found to occur with the production of dark precipitates.

The circumstantial evidence therefore strongly suggests that the oxidative dissolution of gold and other metals from carat gold alloys, in the presence of amino acids secreted or derived from the skin, plays a rôle not only in the wear of carat gold jewellery items, especially rings, watch cases, bangles and watchbands, but also in the production of smudge by such items. Other substances secreted by the skin, and in particular sodium chloride may also be factors in the tarnishing and corrosion of carat gold alloys. Contamination of the skin with sodium chloride, from the handling of common salt or from sea water or sea spray may reinforce the effects of sodium chloride in sweat.

Other Aspects of Gold Smudge Formation

Although metallic abrasion and corrosion are generally recognised (29) as potential causes of smudge formation in the majority of subjects who appear to be susceptible to it, the possibility that medical and biochemical factors may be involved in some instances cannot be excluded.

Thus, 1 case has been placed on record (30) of a diabetic patient whose hands were stained black whenever she handled gold and silver. On treatment with insulin this no longer occurred. However, the black staining reappeared immediately following ingestion of excess of glucose. As yet, this observation has not been followed up.

Allergic Responses to Skin Contact with Gold and Gold Alloys

Although parenterally administered gold salts are a known cause of dermatitis, and there have been reports of dermatitis caused by skin contact with gold (III) chloride and with potassium gold (I) cyanide solutions (31–38), cases of contact sensitivity to metallic gold or gold alloys have rarely been described. Metallic gold, carat gold jewellery alloys and dental gold alloys are widely accepted as non-sensitizing or non-allergenic materials which are safe and inert in contact with the skin or oral mucosa even over long periods of time. Such acceptance is based upon the fact that although millions of people wear or have worn gold jewellery or have, or have had, dental restorations or prostheses made of gold alloys, clinical cases of allergic contact dermatitis to gold are so seldom encountered as to be virtually unknown. Thus Elgart & Higdon (39) were able to describe only 7 cases of gold allergy which had previously been reported in the literature (40–46) and of these, 1 case had not been confirmed by patch testing. The number of such cases which have been described has not grown significantly since then (47–65).

Some aspects of these rare responses to gold which merit attention are the following.

(i) It is unlikely that they could be produced by gold or gold alloys in the metallic state. They therefore indicate that certainly with the rare people who are sensitive to contact with gold, and possibly also with all people to a greater or less extent, gold in both the pure and alloyed form is converted in small amounts, probably by the action of amino acids in the sweat, into soluble form and absorbed into/or through the skin.

(ii) That this is the case has been confirmed by Brown et al. (27) who found gold in amounts of 0.09 and 0.07 mg/g, in 2 samples of skin taken from below gold rings on fingers.

(iii) The ability of gold to move in the reverse direction from blood to skin is well established and skin disorders are a well-documented (66) complication of gold therapy of rheumatoid arthritis. Moreover Brown et al. (27) have referred to a publication (in press) by Sturrock concerning a history of patients who, on starting chrysotherapy, produced rashes specifically in those areas of their skin which had been in contact with gold jewellery. The rashes are apparently different, both in speed of appearance and specificity of site from the skin rashes which are 'normally' associated with gold injections. Brown et al. (27) speculate as to whether those specific rashes may not be examples of skin irritancy resulting from injected gold-reaching parts of the skin already sensitized by absorbing gold.

(iv) In the case of those few persons who suffer skin irritation or dermatitis as a result of wearing carat gold jewellery, the possibility must be borne in mind – even if sensitivity to gold can be demonstrated by patch tests – that this sensitivity may be enhanced by other metals being absorbed by the skin along with the gold. In some cases, the irritation or dermatitis may be caused by base metals alloyed with the gold. Nickel, which is present in some white gold jewellery alloys, may be the offending metal (67).

(v) In contrast to massive carat gold jewellery, items in the production of which gold has been plated over other metals have frequently been identified as a cause of skin irritation. The cause in virtually all cases that have been studied (68) has been either the use of an undercoat of nickel beneath the gold, or the use of a nickel-containing gold alloy as the substrate. Nickel is strongly allergenic.

(vi) In general, gold must therefore be seen as a metal which at least possesses the potential capability of producing skin reactions. That it does so in very rare cases is almost certainly to be attributed partly to its nobility, which hinders the production from it in significant amounts of soluble gold salts capable of being absorbed by the skin, and partly to the very small proportion of persons in whom absorbed gold reaches pathogenic concentrations.

(vii) In view of the above it is indeed remarkable that adverse reactions to gold are virtually unknown in dentistry. This may in some measure be a reflection of the extent to which gold restorations and prostheses are 'irrigated' in the mouth. It may also be a consequence of the almost exclusive use, up to a few years ago, of high gold-content alloys selected in part for their high resistance to tarnish and corrosion.

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Address:

W. S. Rapson
International Gold Corporation Limited
The Corner House
63 Fox Street
2001 Johannesburg
South Africa