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A Permanent Wave Neutralizer: Its Performance and Mechanism of Action

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Synopsis—A bromate-based permanent wave neutralizer, modified by the addition of at least 24% magnesium sulfate (U.S.P.), has been found to improve the stability of waved tresses in water and, more markedly, in air. A determination of its mechanism of action indicated a combination of effects responsible for its beneficial action. Among these effects are: charge neutralization, uptake of the added salt, and re-formation of hydrogen bonds. To be effective, the added salt must be applied concomitantly with the oxidant, thus re-forming both disulfide and secondary bonds at the same time, a process labeled "parallel waving." The modified neutralizer, compared to bromate, appears to produce a greater degree of hydrogen bond re-formation which (together with its other effects) demonstrates how secondary bonding can promote improved waving performance.

Introduction

Permanent waving in its simplest aspect consists of wrapping the hair on a mandrel and then treating it chemically to break down the primary (disulfide) and the secondary (salt and hydrogen) linkages of the keratin, this breakdown followed by the re-formation of these same linkages (1).

In the formulation of solutions for permanent waving, the prime concern has been the ability of reagents, suitable for human use, either to

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sever or to re-form these bonds. In most instances, both types of bonds are broken by a combination of a thioglycolate salt (which reduces the disulfide to sulfhydryl) and an alkali, such as ammonia, which breaks the secondary bonds and permits the hair to become hydrated. The re-formation of the bonds has generally been effected by oxidation, either by air or by a solution, termed a neutralizer, which contains an oxidant (1).

The neutralizing solution ideally should re-form all the previously severed bonds. It is expected to restore at least the disulfide bridges from the sulfhydryl groups. The degree, however, to which this type of neutralizer is capable of re-linking severed secondary bonds is a moot question.

To the extent that the re-formation of the linkages originally severed in the waving process is less than complete, the hair may lose strength and stability in either air or water, or both. Such loss of stability was considerably evidenced by tresses waved with thioglycolate followed by an oxidant-based neutralizer. In water, the tresses contracted and rearranged their curl patterns; in air, they drooped and lost their curl. Since air (dry) stability of hair is said to depend strongly on the hydrogen bonds (2), apparently the waving process would be improved if the oxidant neutralizer could be made to achieve a greater degree of hydrogen bond re-formation.

The question arises whether the neutralizer can be formulated to achieve a greater degree of curl strength and stability. Observations of the performance of a bromate-based neutralizer containing a high percentage of salt indicate that this is possible. The waving performance of such a neutralizer is, therefore, reported in this article together with a study directed toward determining its mechanism of action. These results demonstrate how re-formation of secondary bonds may be augmented by the neutralizer and how this, in turn, increases the stability of the wave.

While searching for substitutes for neutralizing agents usually used in permanent waving, it was observed that a solution of calcium acetate when used as a neutralizer on hair previously waved with alkaline thioglycolate conferred good air stability (or droop resistance) on the tresses; however, these tresses relaxed in water. Those waved with the usual sequence of thioglycolate:oxidant, when placed in water, were resistant to relaxation. The individual hairs, however, tended to unwind and then rewind into the characteristic helical shape. Though resistant to relaxation, these tresses were not as stable as the ideal tress desired, that is, one which in water would not move at all.

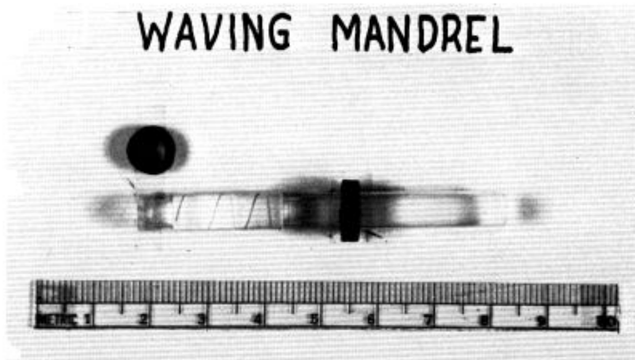

Figure 1. Mandrel used in waving experiments

An attempt was made, therefore, to formulate a neutralizer which would combine the air-stabilizing qualities of the calcium acetate together with the water-stabilizing qualities of the oxidant, the latter improved in the direction of less rearrangement in water. After consideration of the action of various salts, it was noted that a number of these (including those of sodium, calcium, magnesium, and aluminum) in sufficient concentration, produced varying degrees of improvement. On closer examination, however, the sodium salts were not as useful as those of the di- and trivalent metals. Magnesium sulfate (U.S.P.) ($MgSO_4 \cdot 7H_2O$) was ultimately selected as the optimum salt. It is this substance, unless otherwise specified, which is the salt added to the oxidant in the presentation that follows (3).

Methods

Technique of Waving

A plastic rod of 6-mm diameter was notched at each end to permit placing of two rubber washers (19 mm apart) for securing hair in place. A thin helical line was etched on its surface making close to three turns (Fig. 1). Twelve human hairs (virgin, brown European) were glued at one end with Duco Cement®.* The cemented end was slipped under one of the washers, wrapped around the mandrel while adhering to the etched line, and slipped under the second washer. Two inches of hair were left free beyond the washer. After waving and removal from the mandrel, the excess hair was cut at the notch made in the hair by the second washer. Over-all length of tress when straight was 62 to 64 mm; when helical it was 19 mm.

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The mandrel with attached tress was placed vertically in a test tube 18 × 150 mm and a commercial waving solution containing 7% w/v thioglycolic acid adjusted to pH 9.4 with ammonia was added, sufficient to cover mandrel plus about one inch.

After six minutes, the mandrel and attached tress were rinsed five times, with warm (about 50 °C) water.

A commercial neutralizing solution containing 9–11% w/v sodium bromate, with and without addition of 30–36% w/v magnesium sulfate (U.S.P.), was then added, and after eight minutes the mandrel and attached tress were rinsed three times in warm (about 50 °C) water followed three times by cold (about 25 °C) water.

The mandrel with attached tress was dried by rolling in facial tissue and the tress was removed after about five minutes.

Performance Tests

Air Stability

Air stability tests and measurements were done 5 to 10 minutes after removal from the mandrel in order to allow any relaxation or change in shape of the tress to occur first.

Waves were rated by numbers 0, 1, 2, 3:

Wave 0—No loop or curl.

Wave 1—One loop or curl.

Wave 2—Two complete loops or curls.

Wave 3—(Highest rating)—From 2.5 to just under three loops, and, in addition, of "tight quality"—meaning a diameter close to that of the rod.

Distances between Loop Crests (D2L)

This measurement is the linear distance in mm from the beginning of the actually waved hair to the completion of the second loop. Best rating: 12 mm, the actual distance on the mandrel.

Water Stability

After the air stability measurements, the tress was laid horizontally on the surface of a container of water and gently pressed into the water so that it floated freely just below the water's surface. A wave test (WT) rating was then given:

Rating 3—Completely water stable, i.e., unaffected by water. May also be tightened by water, as in some cases following unwinding and rewinding of the tress. Hairs *regular,* i.e., together and not apart from one another. Final shape of tress is helical.

Rating 2+—Unwinding and rewinding in water as previous, but hairs are not sufficiently regular to rate 3.

Rating 2—Slightly straightened by water, but retaining most of curl.

Rating 1 or 0—Nearly (or completely) straightened out.

Distance between Loop Crests in Water (D2LW)

This is a more quantitative value for the water test. The closer it is to the D2L value, the more water-stable.

Vertical Length Wet (VLW)

Tress was lifted from water by tweezers, grasped at the cemented end, lightly touched to facial tissue in order to remove excess water, and its length measured in mm. Most tresses stable in both air and water gave values in the 37–39 mm range. A straight tress measured 62–64 mm.

Inside Diameter (ID)

Immediately after the VLW measurement, the tress was laid down on a facial tissue in such a way that it formed a series of concentric circles lying on top of one another. The ID of this "coil" was then measured in mm. The best diameter was 7 mm.

After-Water Stability (AW)

After taking the ID measurement, the tress, held by the cemented end, was first dipped into water, to allow it to lengthen itself naturally, and then lightly rolled on the surface of facial tissue and allowed to air-dry; its shape and regularity were noted.

The tresses were rated as "excellent," "good," "fair," etc., depending on how close their dimensions were to the original helical contour and on their regularity (Fig. 2).

Repeated Waving of Same Tress

To determine if the benefit given by added magnesium sulfate was retained upon repeated waving, individual tresses were waved six times in succession with at least one day between treatments. Air and water stability values were measured after each treatment.

Serigraphic Measurements

Tresses of 12 hairs were glued at one end and then taped at both ends with small squares of tape to produce a length between the facing edges

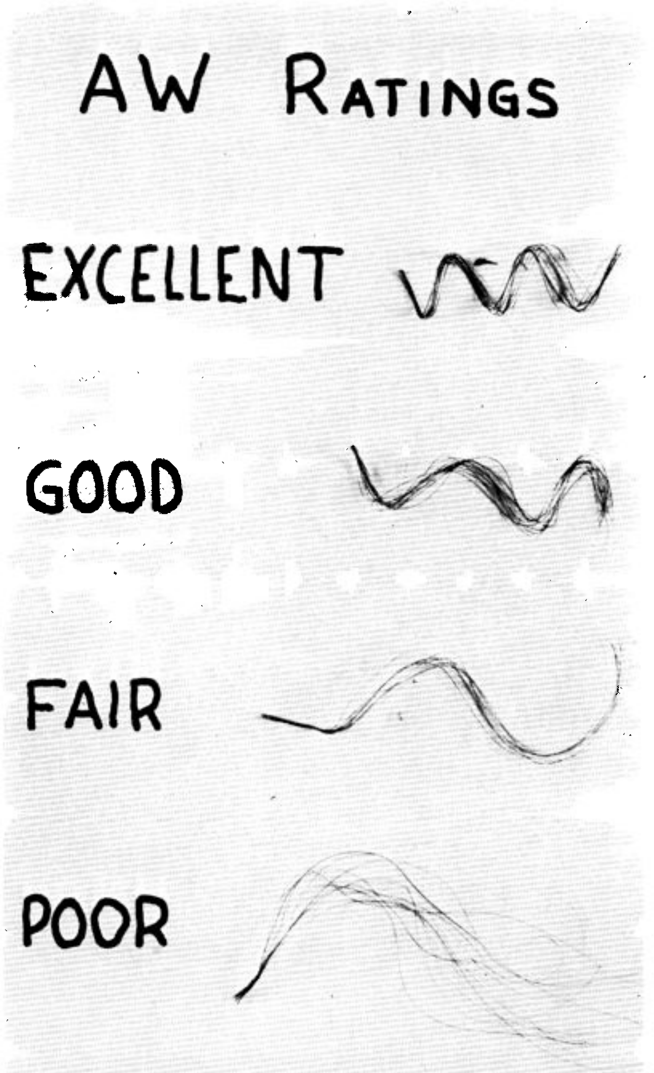

Figure 2. Waved tresses illustrating the AW ratings used in the waving experiments

of the tape of 90 mm. An excess of hair was left at the unglued end to facilitate handling of the tress. These were then extended for 20% of their original length using a Model IP-2 Serigraph.* During extension, the tress was kept wet by draping a folded piece of filter paper (close to 90

* Manufactured by Scott Testers, Inc., Providence, R.I.

mm long) over the hair which was liberally moistened with water by use of a medicine dropper.

To determine the influence of the various waving procedures on the tensile strength of the hair, the tress was extended on the serigraph on one day, treated the next day, and extended again on the following day.

The data were recorded in terms of the load required to extend the tress both before and after treatment. The second reading divided by the first times 100 was considered as the 20% index.

Results

Table I compares the results of performance tests on tresses neutralized with bromate alone and bromate plus $MgSO_4 \cdot 7H_2O$. The addition of $MgSO_4 \cdot 7H_2O$ to the bromate neutralizer resulted in:

a. Higher initial wave values indicating the tress conformed more closely to the wave pattern on the mandrel.
b. High WT values indicating better wave stability in water.
c. Lower VLW values indicating stronger wave formation.
d. Superior AW values indicating better wave stability in air.

The same results are seen after six repeated wavings of the same tress.

The results in Table II show a 27% increase in the 20% index for tresses waved with the neutralizer containing 30% w/v magnesium sulfate (U.S.P.) as compared to tresses waved with the standard bromate neutralizer.

Influence of Salt Concentration and Salt Uptake

It was noted early in this study that the improvement to air stability given by the added salt increased as the concentration of the salt increased, and that for the desired air stability a minimum concentration was required.

This is illustrated in an experiment in which waving performance was judged when increasing amounts of magnesium sulfate were added to a sodium bromate-containing neutralizer. The results are summarized in Table III. Note that the desired excellent stability was not achieved until over 24% of the salt was present.

It had also been observed that ignition of hair waved with a neutralizer containing the added salt yielded an ash termed "uptake," in which the cation of the salt could be chemically demonstrated. In order to relate salt content, performance, and uptake, the same neutralizers listed in Table III were used to wave a series of tresses which

Table I
Waving on Mandrel

	Bromate Only		Bromate with 36% $MgSO_4 \cdot 7H_2O$	
	First Wave	Sixth Wave	First Wave	Sixth Wave
Wave value	1.9	1.6	3	3
D2L, mm	23	23	12	12
WT	2.9	2.8	3	3
D2LW, mm	15	15	14	14
VLW, mm	43	43	39	39
ID, mm	7	7	7	7
AW	Fair	Fair	Good to excellent	Good to excellent

Data represent average of measurements for three tresses.

Table II
Serigraphic Measurements

	Bromate Only	Bromate with 30% $MgSO_4 \cdot 7H_2O$	Significance (P. value)
First load, g	163	152	
Second Load, g	66	77	
20% Index	40	51	0.02

Data represent the average for four tresses.

Table III
Effect of Increasing Amounts of Magnesium Sulfate on Waving Performance and Percentage Ash

	% $MgSO_4 \cdot 7H_2O$						
	0	6	12	24	36	47	58
Wave value	2	2.3	2.3	2.7	3	3	3
D2L, mm	18	17	16	14	13	13	13
WT	2	2.7	3	3	3	3	3
D2LW, mm	17	15	13	13	14	14	14
VLW, mm	40	40	38	38	37	37	37
ID, mm	7	7	7	7	7	7	7
AW	Fair	Fair to good	Good	Good to excellent	Excellent	Excellent	Excellent
% Ash	0.1	0.4	0.4	0.5	1.1	1.0	1.1

Table IV
Effects of a Citric Acid Rinse Between Reductant and Neutralizer

	Bromate Only		Bromate with 36% $MgSO_4 \cdot 7H_2O$	
	Acid Rinse	No Rinse	Acid Rinse	No Rinse
Water Value	2	2.3	3	3
D2L, mm	18	16	12	12
WT	2.3	2.3	3	3
D2LW, mm	15	16	13	13
VLW, mm	40	41	38	37
ID, mm	7	7	7	7
AW	Fair to good	Fair	Excellent	Good to excellent
20% Index	...	...	60	55
% Ash	...	...	0.37	0.56

were weighed and then ignited to constant weight. The residues were weighed and then calculated as per cent ash. These results are also included in Table III.

The results show that the higher the salt content, the higher the uptake. There is a distinct upward break in the uptake between the two neutralizers containing the 24% and the 36% magnesium sulfate, the upper corresponding to the value at which the desired air stability was achieved.

At this point it appeared that the concentration of the salt and the amount of uptake from the solution could be considered as factors to account for the improved air stability.

The Effect of an Acid Rinse between Reductant and Neutralizer

If it is assumed that negative charges in ammoniacal-thioglycolate reduced hair are the sites to which the uptake is attached, it appears reasonable to consider the uptake as cationic. The question then arises: What would be the effect of treating the hair with an acid rinse between the reduction and the oxidation steps?

Experiments were, therefore, performed in which a 3% solution of citric acid was applied to hair for 8 minutes between the reduction (6 mins) and oxidation step (8 mins). Rinsing was done between all the applications. As oxidants, both bromate and magnesium sulfate–bromate were used. The experiments covered waving on the mandrel, serigraphy, and ash determinations. Their results are summarized in Table IV.

The results obtained in these experiments indicate that:

1. The acid rinse lessened the cation uptake by 34%. In addition, the network-like ash characteristic of the salt-bromate neutralizer was not at all evident; only a small clumplike residue was visible.
2. The waving performance on the mandrel, despite the lessened uptake, was somewhat improved. The general range of values was not much changed; without added salt, the AW values remained in the fair range; with salt, close to excellent. The improvement was manifest in a greater degree of regularity.
3. Serigraphically, there is no loss of strength.
4. Although the in-between acid rinse improved the waving sequence when no salt was added to the neutralizer, this three-stage waving sequence cannot be said to approach the over-all performance of reductant followed by bromate-containing magnesium sulfate.

Citric acid could be expected to include, among the possible actions, that of neutralization of the excess negative charges in the keratin. The fact that the acid displaced a significant portion of the cationic uptake permits the conclusions to be drawn that:

1. Part of the mechanism of action of the added magnesium sulfate *is* one of charge neutralization; and
2. Uptake does strongly parallel improvement in waving performance, but it is not a sole operating mechanism.

Dehydration Mechanisms and Hydrogen Bond Re-formation

The question arises: What other mechanism(s) could be involved? The consistent improvement in waving properties throughout a wide range of increasing salt concentration suggested a possible dehydration mechanism.

Two possible dehydration mechanisms were considered: one osmotic and the other a salt-protein interaction in which the water that is hydrating the protein is removed by a salt in sufficient concentration.

In order to determine whether an osmotic mechanism is operating, the vapor pressures were determined of a series of neutralizers in which a number of salts in varying molalities were combined with sodium bromate whose final concentration was $0.67m$. Tresses were then waved utilizing these neutralizers. The effects of the added salt on the AW values are shown in Table V.

In utilizing this approach, the assumption was made that if the effect of the salt were due only to the solution properties (as osmotic pressure) and not to specific salt-protein interaction, then the determination of vapor pressure lowering should correlate with the effect on curl formation.

In Table V the results of the measurements of vapor pressure lowering indicated that this property could not be used to predict the effect of a salt on air stability; there was no indication that a given vapor pressure range or a required vapor pressure lowering could be cited as required for optimum waving results.

The experimental results to this point may be interpreted as follows: The magnesium sulfate in relatively low concentration neutralizes the excess negative charges and brings the keratin closer to its isoelectric point; here, the protein is most easily susceptible to dehydration which is then effected by the salt's relatively higher concentration (4). During dehydration, the hydrogen bonds whose strength and tendency to form are minimal in water itself, have, in the relatively decreased water content (provided by the high concentration of the added salt) an increased likelihood to re-form (5).

Consecutive or Simultaneous Application of the Added Salt with the Oxidant

The favorable results of adding a salt in sufficient concentration to the oxidant raises the question of how the effectiveness of the salt would be influenced by its being applied *separately* to the hair just prior to or following the oxidant.

To answer this, tresses were waved by first reducing them for six minutes with ammonium thioglycolate; these were then divided into two groups which were treated by *either* of the two following procedures:

1. 30% aqueous solution of magnesium sulfate followed by a bromate neutralizer, each for 8 minutes; or
2. A bromate neutralizer followed by a 30% aqueous solution of magnesium sulfate, each for 8 minutes.

Rinsing was done after application of each of the above solutions. The experimental results are summarized in Table VI.

From the tabulated results, it is evident that the tresses in the two groups somewhat resemble one another and that both are quite similar to tresses waved with the salt-free bromate neutralizer. This is especially noticeable in their rather poor AW values.

These results clearly indicate that for the added salt to be of benefit in conferring air stability on the tress, it must be applied *simultaneously* with the oxidant. Apparently, the re-formation of the secondary bonds is facilitated only if done at the same time as those of the disulfide bridges.

Table V
Vapor Pressure and Waving Performance of Bromate Neutralizers with Various Salts

Salt	Molality	Vapor Pressure @ 30°C mm Hg	AW Rating
...	...	30.1	Fair
$MgSO_4$	1.5	29.3	Excellent
LiBr	1.5	29.0	Poor
Mg Acetate	1.5	27.8	Excellent
$MgCl_2$	2.0	25.0	Fair

All neutralizers contain 0.67*m* sodium bromate.

Table VI
Effect of Application Sequence of Bromate and Magnesium Sulfate

	Waving Sequence Following Ammonium Thioglycolate Reduction	
	(1) Magnesium Sulfate (2) Bromate	(1) Bromate (2) Magnesium Sulfate
Wave value	2	3
D2L, mm	17	14
WT	3	3
D2LW, mm	14	12
VLW, mm	37	37
ID, mm	7	7
AW value	Poor to fair	Poor

Data represent the average measurements for six tresses.

Discussion

Farnworth (6) suggested that permanent set in wool, which is analogous to the permanent wave in hair, results from the breakdown *and re-formation* (italics, ours) of hydrogen bonds following the splitting of cystine linkages. Concurrence with this view has been voiced by Whewell (7) and Walker (8). In waving with ammoniacal thioglycolate, followed by oxidation, two of these three mechanisms have been effected, namely, the cleavage of disulfide and hydrogen bonds. The salt-modified bromate neutralizer appears to give improved wave stability, in part at least, by augmenting hydrogen bond re-formation. To the extent that this is true, the third of the proposed three prerequisites for permanent set has been provided.

Whewell, in a remark appended to a subsequent study (9), held that the role of hydrogen bond breakers was complex, but they did seem to increase disulfide scission by bisulfites. He described the action of disulfide breakers as that of a key which opens up the fiber so that hydrogen bond breakers can be effective. The effectiveness of the modified neutralizer makes the reverse reasoning of the previous statement interesting to consider: namely, that the re-formation of hydrogen bonds seems to increase disulfide relinkage and that the substances that restore disulfide linkages act like a key which closes up the fiber so that hydrogen bond re-formers can be effective. It is our observation that the re-formation of both types of bonds must be done concomitantly for the production of the optimum wave stability. The simultaneous relinkage of both types of bonds has been given the term of "parallel waving."

Bogaty showed by carefully chosen experiments (10) that the individual participation of both primary and secondary bonds in the waving procedure could be demonstrated, and, furthermore, that the potential benefits to waving by an effective utilization of secondary bonds (along with sulfur cross links) was yet to be fully realized. Hopefully, this study demonstrates a manner by which this can be accomplished.

Summary

Tresses were set with a bromate-based neutralizer modified by the addition of an amount of magnesium sulfate in excess of 24%. Compared to the results obtained with the unmodified bromate neutralizer, the tresses were superior in air- and water-stability; did not lose their improved performance despite repeated waving; and gave appreciably higher 20% index values when determined on the serigraph.

A study of this neutralizer's possible mechanisms of action indicates that a combination of effects appears responsible for its beneficial action. Among these are: charge neutralization, uptake of the added salt, and re-formation of hydrogen bonds. To be effective, the added salt must be applied concomitantly with the oxidant, thus re-forming both disulfide and secondary bonds at the same time, a process labeled "parallel waving."

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