STABILITY TESTING OF HAIR PREPARATIONS

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In establishing laboratory methods for testing the stability of cosmetic products, four types of product stability must be evaluated. These are chemical, physical, bacteriological, and what can perhaps be referred to as functional stability.

Chemical stability is the absence of any chemical reaction in the packaged product, especially where so-called active ingredients are present. Chemical deterioration or changes in the product often bring about some change in the appearance of the product as well, and may be detected visually. But very frequently chemical changes are not accompanied by visible physical changes, and chemical analysis must be resorted to in order to detect such a change. Typical examples of chemical instability where the appearance of the product is not usually affected are (a) a drop in the thioglycollate concentration of cold wave solutions, due to oxidation and usually detected by iodimetric titration; and (b) the decomposition of solutions of hydrogen peroxide, which is usually detected by a permanganate titration.

The physical stability of a product may be adversely affected by such phenomena as emulsion separation, creaming, pigment settling, clouding or turbidity in clear liquids, discoloration, and precipitation or crystallisation in liquid products. Both chemical and physical changes may be interrelated and a chemical change can and often does cause a change in the appearance of the product. Odour changes can also be included in this group because they can easily be detected by an educated nose.

Bacteriological stability is a third requirement. The ability of micro-organisms to ruin a product is well known, and a product which is not properly protected from the development of micro-organisms usually ends up in the "returned goods department" of the manufacturer.

A fourth and often overlooked kind of product deterioration is what I like to refer to as the functional instability of a product. No product can enjoy repeat sales unless it does the job it was designed to do. Appearance, odour and packaging will not sell a product that does not measure up to the performance claims on the label and in its advertisements. In many instances, if a product does not function properly

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six months or a year after manufacture, the failure can usually be attributed to an easily detected chemical or physical change. But this is not always the case, because occasionally a product will be returned because it does not perform properly, although it did the job when it was manufactured; it looks and smells the same, and routine chemical analysis discloses no chemical change in the product. A chemical change may in fact have occurred, but it is not always a simple matter to determine precisely what slight and subtle change has taken place. Examples of functional instability are: the aqueous wave set which is still bright, viscous, stringy and pleasant smelling, but flakes badly when dry on the hair—which it did not do when it was freshly made. Another is the oxidation type of hair colouring that looks and tests the same as it always did, but it will no longer colour the hair—or it does colour the hair, but not in the original shade.

TIME AS A DETERMINING FACTOR

The point to make here is that even if a product passes all the usual accelerated stability tests it should be tested frequently by actual use, to be certain that it does the job it was designed to do. The actual sample that was used for the stability tests should be used for the performance tests and compared with a sample of the product that did not receive the accelerated stability tests.

In formulating a new cosmetic product adequate shelf-testing is a vital necessity and, although accelerated stability tests have great value, there is still no substitute for time.

Accelerated stability tests are not infallible and, if the maximum benefit is to be derived from them, an understanding of their limitations is essential. I have had the exasperating experience of seeing a product pass every accelerated stability test, but samples from the same batch that were not put through the tests went bad. It is not unusual to have a product pass all stability tests, only to have it develop some defect many months later. I can recall several such examples, but one will suffice. A company manufactured a cosmetic preparation in the form of a thick, pearly, liquid emulsion—a beautiful product which had passed all the stability and shelf tests in the laboratory. Several months after distribution of the product began, it started to come back because the emulsion was speckled throughout with large white grains. Microscopic and other tests identified these specks as crystalline clusters of cetyl alcohol. However, the laboratory was never able to bring about this condition using good samples from the same batch that went bad.

What cosmetic chemist has not had the experience of formulating a new product in the laboratory, only to find that the first production batch or even a pilot batch, did not have exactly the same properties? It is for this reason that a laboratory-prepared sample of a product is not desirable for use in any stability testing programme. Two or more pilot or production batches, preferably made from different lots of raw materials, should be used for the final tests if they are to have any real value.

With these facts in mind, and with an understanding of the limitations of accelerated stability tests, I can go on to discuss such tests for specific hair preparations. Raw material control will not be included, although its importance should not be minimised. The stability or instability of a cosmetic product very often depends upon the quality and control of the raw materials used.

I shall limit my remarks to three very popular types of hair preparations, namely cold wave solutions, shampoos, and hair-setting cosmetics. Dr. William Colburn has already ably discussed the stability testing of emulsions (this *Journal*, Vol. 2, No. 3), and so I shall not attempt to discuss emulsified hair creams and lotions.

TESTING COLD WAVE PREPARATIONS

Most cold wave preparations on the market to-day consist essentially of an aqueous solution of thioglycollic acid (usually as the ammonium salt) and an excess of alkali to bring the *p*H to about 9·0–9·6. They may also contain a wetting agent to facilitate penetration into the hair, a clouding or opacifying agent to impart a milky white appearance to the product, perfume, and colouring matter. The solution is usually packaged in 3 or 4 ounce bottles that are either sealed with a paraffined cork plus a metal cap or a plastic cap that has a vinylite liner.

There are a number of difficulties that can occur in a packaged cold wave solution :

1. The thioglycollate concentration can drop. The active content of thioglycollate salt can be determined by iodimetric titration. This drop can be due to inferior raw materials or to a defective seal. Thioglycollic acid is easily oxidised to dithioglycollic acid, especially in alkaline solution in the presence of traces of metals, such as copper or manganese, which catalyse the oxidation.

2. The *p*H can drop. The *p*H of cold wave solutions must always be kept within a rather narrow range in order that the solution shall function properly when applied to the hair. Reaction of the alkali with the wetting agent or with the emulsified oils may cause the *p*H to drop.

3. Discoloration of the liquid may occur. A pink colour is caused by iron, which may have been present in one of the raw materials, in dirt or dust in the bottle, or may have got into the solution by corrosion of the metal cap. Only one part of iron in four million is needed to turn the solution pink, so the importance of keeping cold wave solutions free from iron is obvious. A yellow discoloration may appear, especially where a poorly paraffined cork has been used to seal the bottle. The tannin becomes extracted from the cork, resulting in the off-colour.

4. Breakdown or separation of the emulsified oils. This can be a very serious problem in cold wave solutions that have a white or milky appearance. The clouding agent must be selected with great care and the finished product subjected to thorough testing in the laboratory.

5. Perfume difficulties. Perfumes have not been too successful in covering the ammoniacal and thioglycollate odour of cold wave solutions, but they are used in many preparations. Although the odour character of the perfume may change with age, a far more serious problem occurs when the perfume oil is thrown out as small globules.

6. Fading or change in colour when dyes or other coloring matters are used. Since cold wave solutions are powerful reducing agents, many dyes which may be used to colour the solution are unstable. Very few of the certified colours show satisfactory stability in cold wave solutions, but accelerated laboratory stability tests will usually weed out the dyes that are unsatisfactory.

7. Formation of sediment or crystals in the solution. These are usually insoluble organic sulphur compounds and may be found when an inferior grade of thioglycollic acid is used.

Any method of accelerated stability testing of cold wave solutions must be able to evaluate both chemical and physical changes in the product. Two significant chemical changes which may occur are a fall in the *p*H value and in the thioglycollate concentration. And changes which may alter the appearance of the product are emulsion breakdown, perfume separation, or discoloration.

Bottled samples from each batch of cold wave solution should be shelf-tested for at least a year and examined frequently to check for emulsion breakdown or discoloration.

They should be assayed for thioglycollate by iodimetric titration and the *p*H accurately determined. Samples can also be tested for heat stability at 100° and 120°, and cold tested at 35° to 40° F. Both heat and cold tests can run up to 30 days and longer, after which the solution is again assayed for thioglycollate and the *p*H determined. Accelerated shelf tests, such as sustained heat at 100° to 120°, will usually reveal whether or not the emulsion, perfume, wetting agent and colour are stable and compatible in the presence of alkaline thioglycollate.

During the early years of cold wave development an accelerated test that was occasionally used was to bubble air through a cold wave solution and assay the solution at frequent intervals. When ammonia was used as the alkali the *p*H continued to drop, due to loss of ammonia, and the rate of oxidation decreased. When fixed alkalis were used, the rate of oxidation often indicated the presence or absence of trace metal catalysts or the effect, if any, of the various additives such as perfume, clouding agent, wetting agent, etc., on the rate of oxidation. An accelerated test that I have often used was similar to this but more precise. In an apparatus similar in appearance to a Van Slyke amino nitrogen set-up, a measured volume of finished cold wave solution was mechanically shaken with a measured amount of oxygen and at intervals a sample was drawn off and the rate of oxidation determined. Whole series were run on various formulations to eliminate those materials which tended to catalyse the oxidation of thioglycollate to dithioglycollate.

Cold wave preparations are given a milky white appearance by the addition of an oil or resin generally added as a concentrated emulsion or resin dispersion. Of course, such an emulsion must be stable and compatible with alkaline thioglycollate. Any accelerated test generally used for dilute emulsions can be used here too. Heat and cold tests, alternating heat and cold tests, and mechanical agitation, all have value. An accelerated test that is often used, especially for dilute emulsions in the presence of electrolyte, is to centrifuge the product at speeds from 1,500 r.p.m. upward. The more unstable the emulsion, the greater the creaming or separation when centrifuged.

It has been my experience that cold wave preparations properly formulated from high-quality raw material showed no appreciable change in both chemical properties and appearance even after several years.

Dealing with Shampoo Problems

The manufacture of stable, trouble-free shampoos might appear to the uninitiated to be a simple matter—and perhaps it was, when the shampoos were all clear, liquid soap preparations. Now we have, in addition to soap shampoos, synthetic detergent shampoos and the so-called oil shampoos. These, in turn, may appear as milky shampoos and pearly shampoos, egg shampoos and beer shampoos, concentrated shampoos and powder shampoos, cream shampoos and clear shampoos, deodorant shampoos and colour shampoos, chlorophyll shampoos and curl shampoos and, more recently, pressurised foam shampoos. And each one poses its own special problems.

If you were to ask "What can go wrong with a shampoo?" my answer would be, "Almost everything." Clear shampoos cloud up, viscous shampoos thin out, milky shampoos separate, pearly shampoos settle, egg shampoos coagulate, and cream shampoos either set too hard or become soupy. These are just some of the problems that arise: there are many more.

Two very important determinations that are frequently made on most shampoos are the *p*H and viscosity. A change in *p*H usually means trouble ahead and so this value should be checked often and especially after all accelerated stability tests. A reliable and rapid routine method for determining the viscosity of liquid shampoos is by use of a plastic viscosity cup with a fixed and accurate aperture. The time, in seconds, to fill a 60 ml.

receiver at 80° F. is the viscosity value that is used. The rotating spindle type of viscosimeter such as the Brookfield instrument is not satisfactory for viscous liquids that tend to be thixotropic. As the spindle rotates, the liquid in contact with the rotating spindle thins out and a constant reading is unobtainable.

A very important test for all clear liquid shampoos, whether of the soap, detergent or oil types, is the cold test. Not only is the cloud point determined but also the temperature at which the liquid becomes clear. These two values are not always the same, especially where the shampoo contains sodium lauryl alcohol sulphate. This particular detergent, which is extensively used in shampoos, is not too soluble and tends to crystallise out of solution in the temperature range of 45–55° F., but, what is still worse, is that it might not redissolve until the solution is warmed to 70 or 75° F. These temperature values will vary with the concentration and composition of the shampoo and must be carefully checked.

Milky or pearly liquid shampoos may settle or separate, and oven tests at 100° and 120° F., centrifugation, and exposing the shampoo to prolonged vibration, are all useful accelerated stability tests. One of the basic qualifications of a good cream shampoo is that it should always have good texture and consistency, irrespective of the temperature to which it has been exposed. Freezing, chilling to 35°–45° F., prolonged heating at 100° to 120°, are among the accelerated tests frequently used. After these tests the shampoo is permitted to reach room temperature and then carefully examined for any change. A very valuable tool in the examination of cream shampoos is the microscope. Shampoos of this type usually are a complex suspension and emulsion, and changes in crystal structure and particle size after subjecting the shampoo to accelerated stability tests is often an indication of impending difficulty. Prolonged vibration is also a useful test.

Egg shampoos, still enjoying considerable popularity in the United States, contain either whole, frozen or dried eggs and should be tested for heat stability at 100° and 120° F. The protein is very easily denatured by heat and may coagulate in the shampoo.

White milky or cream shampoos have a tendency to become yellowish upon standing for several weeks or months, especially if they contain unsaturated fatty acids or alkanolamines. Discoloration should be watched for in all the samples that have been put through accelerated stability tests. It is good practice to test unperfumed samples of the shampoo along with the perfumed samples. If discoloration results, it may be due to the perfume, which can adversely affect the shampoo in other ways as well.

Many shampoos are subject to bacterial contamination unless adequately preserved. Shelf-testing the product and waiting for micro-organisms to appear just won't do, and the only way to reach a quick and decisive answer is to use bacteriological methods of evaluation. This is done by inoculating the shampoo with moulds, bacteria and sewage organisms which have been found to contaminate shampoos, and examining the shampoo for colony growth or gas formation.

The packaging of shampoos does not pose any serious stability problems, with the exception of cream shampoos in collapsible tubes. The quickest way to determine whether or not the product will corrode the container is to oven-test it for 30 30 days at 130° F.

Testing Hair Fixatives

Preparations to hold the hair in place, especially some of the newer types, have grown in popularity and include, in addition to the brilliantines, oil emulsions and pomades—a variety of hair setting preparations based upon gums, resins and proteins. The aqueous preparations are generally clear, dilute solutions of gums or proteins and may be thin fluid preparations or viscous, stringy solutions such as those based on gum karaya. Accelerated tests are useful here, especially those which might induce precipitation or turbidity. These products readily support the growth of micro-organisms if not adequately preserved.

Concentrated wave set preparations are manufactured for beauty shop use and consist essentially of an alcoholic suspension of a water-soluble gum, plus other additives. This concentrate is added to water to make a product ready for use. The problem or difficulty that must be looked for here is the caking of the suspended gum so that the concentrate cannot be poured out of the bottle. Two useful stability tests are prolonged vibration and oven-testing at 90° F.

Non-aqueous hair sets are formulated to be sprayed on the hair and are either packaged in a polythene squeeze bottle or as a low-pressure aerosol. These products must remain clear without the formation of any sediment, precipitate or crystals which may clog the spray head or valve. The aerosol preparations are best oven-tested at 130° F. for a period of 30 days, the can being then examined for corrosion.

These hair set preparations should always be checked for functional stability by using the product on live models. The film deposited on the hair must dry quickly, must not flake off, must not be sticky or rough. A simple routine test is to spray the liquid on a flexible sheet of clear plastic and examine the film for tackiness, flexibility, clarity, etc.

Successful cosmetics are the result of:

(1) Rigid control of raw materials.
(2) Careful formulation.
(3) Meticulous care in manufacture.
(4) Maintenance of close tolerances in the finished product.
(5) An exhaustive testing programme, both in the laboratory and in the field.