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Techniques for evaluation of nail enamel

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Synopsis

Appraisal of nail enamel entails examination and measurement of several properties. They include flow characteristics, compatibility of constituents during drying, the rate of drying of films, and their resistance to soap and detergents. Nail lacquers should be carefully tested to make sure that they meet the performance specifications which have been set up by both marketing and technical executives. The judicious selection of testing methods and the correct interpretation of data are vitally important to the development of improved nail coating formulations. The performance of a nail enamel and its components is of primary concern to the lacquer chemist, he must prescribe the tests, interpret and refine the data while recognizing their overall significance, and apply conclusions based on the information obtained in the tests. The following physical parameters of nail enamel compositions are examined and measured along with their respective performance characteristics: adhesion, brushability, color and color stability, detergent resistance, drying qualities, durability, film thickness, flexibility, flow, gloss, storage stability, water resistance and wear.

INTRODUCTION

A recent interview among women readers of SELF Magazine (1), points out that the main factors influencing purchase of nail enamel were pleasing color, protection, wear, shine and ease of application considerations. A laboratory evaluation of experimental formulations will entail the examination of these and other properties. These include flow characteristics, compatibility of constituents during drying, the rate of drying of films, their resistance to soap and detergents, as well as other special performance evaluations.

DISCUSSION

Nail enamels, prior to release from the manufacturing plant, should undergo rigid control analysis. The following tests should be undertaken on all batches of nail enamels to determine the quality of the product: abrasion resistance, adhesion, application, color, density, drying time, flexibility, flow, gloss, hardness, nonvolatile content or solids, settling, viscosity, water content, water and detergent resistance.

ABRASION RESISTANCE

Nail coatings come into direct contact with other objects. The abrasion resistance of a coating (its ability to resist mechanical wear) may then largely determine the length of its useful life. Abrasion resistance of a test coating can be evaluated by periodic examinations performed while on the nail. However, the time to produce meaningful results would be excessive and controls difficult to obtain. The use of a Taber Abraser or similar instrument is used to measure abrasion resistance through the action of two resilient abrading wheels which a.e made to rub the coated surface. The nail enamel coating is applied to a special four-inch-square steel panel having a center spindle hold. The panel is placed on a turntable operating at a constant speed. Two abrading wheels, each 3/4 in. wide, are fixed on each side of the spindle and in contact with the coating surface. A load of up to 1000 g may be placed on the wheels in addition to their own 250-g weight. The direction of the abrasion pattern developed by the one wheel is from the outside to the center and by the other wheel from the center of the panel to the outside. A tachometer is provided to count the number of turntable rotations. Between the wheels, a vacuum device acts to remove loose particles abraded from the coating. With wheels of appropriate abrasive capacity in place under a suitable load, the instrument is operated for a specific number of cycles or until a portion of substrate is exposed. Results may be reported either as the number or cycles to failure per mil of film thickness or as the weight loss in milligrams per 1000 cycles.

Utimately, any nail enamel must be evaluated on nails for wear resistance. For this evaluation a large panel of subjects is employed. Usually, an experienced manicurist applies both the test lacquer and a control on alternative fingernails of the subjects. The enamels are worn for a test period of one week, and the nails are examined daily and the condition of the lacquer recorded. This test will indicate large differences in wear resistance (2). Small differences may be obtained by using large numbers of subjects and setting up a statistical design of the results.

Since the ability to resist mechanical wear may largely determine the length of a nail enamels useful life the aformentioned abrasion resistance evaluations are necessary and somewhat indicative of an enamels integrity.

ADHESION

An efficient coating, must adhere firmly to the nail surface. A striking color or a superior wear resistant polish is relatively useless unless adequate adhesion between the coating and the nail is achieved. Three methods are generally employed to measure this property. The cellophane tape adhesion test (particularly appealing because of its simplicity) and the use of a Hoffman scratch adhesion unit, which records the grams loading needed to scratch a film coating from the substrate glass plate. In the tape adhesion test, the coating is deeply scribed with a razor blade in the shade of a Greek letter lambda or another figure. This cut is made 1 in. high and 1/2 in. wide at the base. A piece of ordinary 3/4-in. cellophane tape, several inches long, is laid over its entire surface with a hard rubber eraser. A tab large enough to be grasped firmly with the fingers is left well above the figure. The tape is then removed by pulling rapidly and evenly toward the bottom of the test panel. An arbitrary numerical rating from 1 (complete failure) to 10 (perfect adhesion) is assigned to the test film depending on the proportion and pattern of any coating removed within the scribed area. Instead of a lambda, a cross-hatch pattern may be made in the coating. Tape is applied and removed as above. An estimate of the percent of coating removed (from 100% to 0%) is an indication of the adhesion of the nail coating.

The Hoffman Scratch-Hardness Tester, consists of a four-wheeled carriage, a scale arm graduated from 0 to 20 that is attached permanently to the carriage in a counter poised condition about the pivot axis, and a scratching tool with a sharp circular rim mounted at 40° to the flat test surface. Riders are attached to the scale arm at the numbered positions. The carriage is held down firmly by hand and moved in the opposite direction to cause a trailing scratch. The large standard rider loads 100 g. per division, while the small quarter rider loads only 25 g. per division. This small rider may be used for making low-range measurements involving small increments of pressure, or it may serve as a vernier with the large rider in making more precise medium-range measurements. Scratch-hardness of a coating is expressed as the force necessary to cut through the film to the substrate while adhesion is expressed as the force required to scrape a path through the film when the stylus begins its motion on the uncoated portion of the panel. A third test method involves the use of an Arco Microknife (3). The adhesion of a lacquer is tested by the parallel-groove method. Successive cuts to the substrate are made with the distance between cuts decreasing by increments of one mil until lateral thrust dislodges the coating. Adhesion is expressed as the widest groove spacing where film removal occured. Determining the force necessary to cut through the film to the substrate constitutes a hardness set.

Finally, a practical test for measuring film characteristics of nail lacquer for adhesion and hardness may be done by using a clear glass panel and a Bird Film Applicator (Bird & Son, Inc., East Walpole, MA 02032) to apply 3-mil wet films of the standard and production batch. After 4–5 hours the films are scraped with a knife which has a slight curve toward the end of the blade. The knife is used to scrape a groove through the film. The scraping is done, holding the knife 90° to the glass panel. Both the resistance to the knife and the appearance of the groove in the lacquer film differentiates the films. A smooth groove that is produced with little resistance indicates the film is too soft. A groove that is produced with finely "feathered" edges along the length of it is normal, as it shows good adhesion. A groove that shows jagged edges, and the material that is scraped off is rather powdery, indicates a film that is too hard or brittle. It is advisable to change standards about once each year since nail enamel loses some of its hardness over a long period of time. The practical test is the one most often employed in the nail enamel laboratory but lacks the sophistication necessary to compare different formulas for adhesion and hardness. It is best to utilize 2 of the 3 methods for accurate results.

APPLICATION

Application to one's nails is the most reliable test method in this case. Checking for evenness and smoothness of brushing as well as streaking should be examined. Before applying a nail lacquer, moisture and traces of oil or soil should be removed from the nail surface to ensure good adhesion and gloss. The thickness of the film governs its wear resistance and gloss. It is desirable to obtain in a single application as thick a film as is practical, from the view of ease of application and rate of drying. Most lacquer requires two applications to obtain a film of required thickness. The film thickness for a single application will depend on the non-volatile components and the viscosity of the lacquer as applied. When one coat has been applied, the first film must be completely dry before the second coat is put on. Some marketers feel that a low viscosity, easy applying enamel is preferred whereby two or three thinner coats are required in order to provide a chip resistant colored film. Application of the standard on the middle finger and batch on immediate fingers to the right and left is done with two coats. Note comparisons. The batch should not be too thin or thick; either characteristic could cause brush marks.

COLOR

A simple check of color and opacity can be made by a pour of both batch and standard onto a glass plate (opal for creams, clear for pearl shades). The plate should then be set vertically so that both pours flow down with edges touching each other. Samples of standard and batch should be compared for color in current nail enamel bottles. Comparison of colors on the nail is similar to the application test previously mentioned. Color should be checked in North daylight or under a Macbeth Daylight Lamp (the Macbeth Corporation, Box 950, Newburgh, N.Y. 12550). An alternative method is to compare the colors on the two thumbnails, holding them side by side, moving the thumb with the standard first on the right, and then on the left. Artificial acrylic nails have been utilized as well for matching comparative shades.

Color strength is evaluated by comparing the standard and batch applied in a 3-mil-thick wet film on a black and white Morest Chart (4). A 3-mil Bird Film Applicator is used to apply nail enamels to the Morest Chart (The Morest Company, Inc., 101 Broad Ave., Fairview, N.J. 07022). A liquid puddle, approximately 3/4 in in diameter, of both the standard and the batch are poured on the upper area of the Morest Chart, side by side, with the standard on the right, and then the Bird Film Applicator is pulled across the surface with a smooth continuous motion, to spread both liquids, at once, into two 3-mil films, side by side. A vacuum suction plate may be used to prevent charts from curling, and causing uneven films. Similar colors should have similar coverage, or hiding power or opacity. Color stability test may be performed and accelerated aging and weathering effects is simulated by storing samples in a 140°F oven. Color is measured against the Parlin Color Standard (ASTM Method D 365). The method employing the Bird Film Applicator and Morest type Chart is more definitive and critical than the glass plate or artificial nail method.

DENSITY

The density of nail enamel, in English units, is determined conveniently by use of the weight-per-gallon cup. This metal cup, calibrated to contain 83.2 ml is filled with test material. When the cover is put into place, a volume in excess of 83.2 ml is forced through a small hole in the top. This excess is wiped off and the vessel weighed. The density in pounds/gallon is calculated as one-tenth of the difference between the cup weight in grams when full and when empty.

DRYING TIME

The application and performance properties of a nail coating depend greatly on the volatility characteristics of its solvent system and therefore on its drying time. A thin layer of lacquer is spread or flowed out on a clean and clear glass panel and observed. The time taken to dry is measured with a stop watch, and checked by pressing the film with a finger, until no mark remains on the surface. This may be done by application of wet films comparing standard against batch using a 3-mil Bird Film Applicator. The two films should be checked by finger tips after about 5 min. The two films should be dry to touch at approximately the same time (within 45 s of each other). Dry-to-touch is the condition at which the film may be touched with a clean fingertip without the resultant transfer of any material to the finger. The total time for achievement should be in the range of 8–10 min, depending upon temperature, humidity, air movement and total solids. Films should be applied under controlled temperature and humidity conditions at 25°C and 50% relative humidity to a completely non-porous surface, in order to standardize this technique. A smoother coat of enamel may be brushed on the nails and dried at room temperature. The film must be dry with no blushing within a specified time ie. three minutes maximum. There are a few marketers that require the enamel to dry quick enough so that the second coat may be applied immediately after the last finger of the second hand is brushed with the first coat.

FLEXIBILITY

Flexibility of the nail enamel film can be measured on a mandril set in accordance with ASTM Method D-1737-62. Briefly, a coated steel panel is placed on its back against a cone or cylinder and then is bent to conform to this shape over a mandril rod of known diameter in a circular arc. The coating is examined for cracking, flaking and loss of adhesion to the substrate against a suitable standard which has undergone the same tests. This method will usually point out inflexible coatings but since the shape of individual nails vary this test alone should not be used to evaluate nail lacquer films flexibility.

FLOW

One of the most important characteristics that a coating should possess is flow or film smoothness. Flow is dependent on the solvency and volatility of the solvent system used. Proper solvency and balanced volatility rate insures a smooth dry film. Flow evaluations are usually subjective when comparisons are made against a standard. Application of enamel is made by pouring from about 1.5 in. to a glass plate and then raising the plate to vertical. The film is observed with a magnifying glass of approximately 5 power. The film should reveal no presence of foreign matter, coarse particles or pinholes.

GLOSS

Gloss comparisons may be made by the flow pour method previously described. This is a visible observation. Gloss comparisons may be made visually by comparing standard and batch on a Morest Chart as in the color tests previously described. Finally, more critical determination of gloss can be evaluated on a glossmeter such as the Glossgar® portable glossmeter (Gardner Laboratories, Inc. Box 5728, Bethesda, MD 20014). Gloss depends upon pigment concentration, solids composition and solvent composition of the nail enamel. An incandescent light is directed at a 60° angle toward the test specimen which has been applied to a Morest Chart. A photosensitive device is provided to measure the light reflected from the test coating at a 60° angle. The light flux is then indicated numerically on a galvanometer. The difference between 100% reflection and the reading obtained represents the incidence light absorbed by the coating or scattered at angles other than 60° by irregularities of the coating surface. Gloss is often defined as the percent of luminous reflectance from a specimen, so gloss readings must lie between zero and one hundred. Instruments must be calibrated to this condition with known standards. Use of the glossmeter is the most preferred. It is the only way that small differences in gloss may be measured. Visual comparisons may only determine if a sample has good or poor gloss when compared to a standard.

HARDNESS

In addition to the methods reviewed under the section on adhesion a simple comparative test is one in which a pour on a glass plate can be scratched with the thumbnail. A harder coating is generally considered to be superior in general performance providing that the flexibility, impact resistance, adhesion, and other properties are equal. Two methods of film surface hardness most commonly used in evaluation of nail enamels are the Sward Rocker and the Tukon Microhardness Tester. Films of 0.0006 in. should be cast on a glass plate and dried for 48 h at 25°C and an additional 2 h at 71°C. The films should be conditioned for an additional 48 h at 25°C before testing with the Rocker. The Rocker consists of two 4-in. metal rings spaced 1 in. apart, a gravity bob for regulating the oscillation frequency or period of the moving system at 1.2 s and a rider on the horizontal nameplate for adjusting the zero point of the balanced Rocker. In order to make a hardness test, the Rocker is placed on the leveled surface and set in motion. The total time required for the amplitude of oscillation to decay by a fixed amount corresponding to a certain number of complete oscillations (not swings), is a measure of the hardness of the test panel or specimen. A greater number of rocks will be recorded for a harder film than for a softer one. The Tukon Microhardness Tester consists of a load applicator, and indenter, and a microscope fitted with a movable stage. To conduct a test, a coating of specified film thickness is applied to a rigid substrate. After the film is dried for a given period, a load is placed on the surface of the coating for approximately eighteen seconds through a pyramid-shaped diamond. Temperature and relative humidity during the test run are kept constant at 25°C and 50%, respectively. The resultant permanent impression made by the diamond is measured with a filar micrometer and the length of the identification is converted to a Knoop Hardness Number (KHN). This number relates the applied load in grams to the unrecovered (approximate) projected area in square millimeters. Knoop Hardness Numbers increase in magnitude with increasing film hardness. Again, as in the adhesion test previously described the thumbnail test can only determine comparative hardness. In order to obtain accurate measurements a

Sward Rocker or the Tukon Microhardness Tester should be used. Either method requires some experience to obtain consistent results. Lastly, due to varying amounts of pigments and pearls present in different shades, the hardness as determined by the Sward Rocker will vary from shade to shade. A range between 8 and 11 oscillations is normal.

NONVOLATILE CONTENT OR SOLIDS

Solvents are used in nail lacquers to dissolve the solid components and subsequently to deposit even films. Although the solvents leave the wet film by evaporation and are usually not recovered, they significantly affect the application, appearance and durability of the film. Despite this they add essentially nothing to the volume of the film deposited. The solid components play the primary role. The concentration of solids in the coatings is the factor which determines to the largest extent the amount of coverage that can be obtained. There are many methods for determination of the solids but the "dish method" is generally accepted. A laboratory analytical balance sensitive to .01 g is required, as well as a ventilated laboratory oven. Pour approximately 1 to 2 g of the nail enamel into a tared weighing dish, approximately 2½ in. in diameter. The exact weight of the sample is then determined by rapidly weighing the dish and sample. The dish with the sample is then placed in a ventilated laboratory oven at a constant temperature of 105°C ± 2°C for 2 h. The dish is removed, placed in a dessicator, allowed to cool to 25°C. Weigh the dish with the residue and subtract the weight of the empty dish to determine the amount of non-volatile solids. Divide the residue weight by the weight of the sample to obtain the percent solids content. The solids, as formulated, is approximately 29% for both creme and pearl nail enamels. Since some of the plasticizers in the enamel evaporate in this test, laboratory determination of solids should range between 27–29% for a 29% solids formulation. Samples should be analyzed in duplicate or triplicate on each batch tested.

SETTLING TEST

A quick test to determine whether a suspension nail enamel will settle in a relatively short period of time is to subject a firmly sealed sample to temperatures of 40°C and 50°C for 24 h prior to release from the manufacturing plant. Samples should be analyzed in duplicate. There should be no visible settling of solid material in the bottom of the tubes. This test is especially important for enamels containing bismuth oxychloride and mica synthetic pearls. Tests may be run at these elevated temperatures for many weeks to determine stabilities on nail enamels. The correlation between oven and storage room temperature stabilities are often poor due to evaporation of solvents, decomposition of nitrocellulose, and other phenomena which occur at elevated temperatures. Still comparative results may be obtained among different formulations and some predictions on storage stability of samples may be determined. Nail enamels exhibit stability at room temperature anywhere from three months to one year depending upon the amount and type of colored pigments present as well as the manufacturer.

VISCOSITY

The measurement of viscosities of suspension nail enamels is not as precise as the old style non-suspending type. Variations in the technique and procedure will produce large variations in results. No one procedure is correct, but the procedure must be standardized. The following suggested procedure is based on ASTN-D-2198-58: "Standard Method of Test for Rheological Properties of Non-Newtonian Materials." This test method has been modified for suspension type nail enamel so as to provide a standard test method which is not too time consuming. The instrument preferred is a Brookfield Viscometer, (Brookfield Engineering Laboratories, Inc. 240 Cushing Street, Stroughton, MA 02172) Model LVT or Model LVF, Spindle #3, equipped with a helipath unit, so that the rotation is read in cps, while the spindle is being lowered into the enamel. The sample size should be 200 g in an 8-oz closed jar. Jar should be covered as much as possible during the running of the viscosity to minimize solvent evaporation. Sample should be aged at least 8 h at 25°C before performing the out lined test. At 25°C, shake very vigorously ten times. Start timer, insert the spindle into the sample to the scored line, with the motor running at 60 RPM. Have the spindle in the correct position in less than one minute. Read the instrument at the end of ten minutes, then switch the speed control to 6 RPM and read the instrument again at the end of another ten minutes. In order to convert the dial readings to centipoise, multiply by the following factors: 60 rpm × 20; 6 rpm × 200. The viscosity-thixotropy relationship of cream nail enamels should be about 375-500 cps. at 60 rpm, #3 spindle, at 25°C. The high speed reading may be considered the viscosity while the second viscosity reading is determined at 6 rpm. The difference in both readings indicates the thixotropy of the enamel—the property that enables the lacquer to suspend pigments and pearlescent materials. The viscosity of pearl nail enamels should be approximately 400-600 cps, at 60 rpm, #3 spindle at 25°C. The reading at 6 rpm for cream and pearl enamels based on guanine should be at least 150 cps higher and at least 200 cps higher for synthetic pearl essence. Base coats, top coats and clears are virtually newtonian liquids and have the same viscosity at both speeds. Often times a Ford viscosity cup run according to ASTMD 1200 is used for the aforementioned products. To obtain a measurement, the cup first is placed on a level plane, and the orifice is closed with the finger. The sample, approximately 100 ml, is poured into the cup until it overflows into the rim provided. A level fill is obtained by drawing a straight edge across the top of the cup to remove excess liquid. A timer is started when the finger is removed and is stopped at the first break in the stream of liquid flowing from the cup orifice. This interval of time, to the nearest 0.2 s, is reported as a measure of the liquid viscosity. The No. 4 cup, for viscous liquid, has an orifice of diameter 0.162 in. and is most often utilized. Busch, et al. found a significant relationship between the application properties of a nail enamel and its rheological requirements (5). It was found that application to the nails involves very low shear rates and low shear forces.

WATER CONTENT

If water is present in substantial quantity as an impurity in solvents and diluents, the shelf life and performance of a finished lacquer can be affected seriously. Water content is determined chiefly by the Karl Fischer procedure and modified by ASTM D 1364. A sample of suitable size is dissolved in a flask containing pyridine and ethylene glycol and then stirred vigorously with a magnetic mixer. The Karl Fischer reagent, which contains iodine, sulfur dioxide, pyridine and methanol, is slowly added from a burette. A series of chemical reactions involving any water present takes place. When all water has been consumed a brown color developes due to the presence of excess iodine. This same end point may be obtained more precisely by an electrical method. Either way, the water content may be calculated from the amounts of the sample and reagent used.

WATER AND DETERGENT RESISTANCE

A water immersion test is used to determine water resistance of a lacquer. A 0.0006-in. film on three glass plates should be applied and dried in an oven at 25°C for 24 h. The plates should be removed and placed in a dessicator for another 24 h and then removed and weighed to the nearest 0.10 mg. The plates should then be immersed in a water bath containing distilled water at 37°C for 24 h. The panels should then be removed and dried by placing the plate between absorption paper and reweighed. They are again accurately weighed and the loss in weight computed as percent of the original weight of the sample.

Detergent resistance may be determined by ASTM D 1647 by the following method: A specimen of each enamel is prepared by dipping a test tube in the lacquer. The test tubes are inverted and supported on vertical pegs during the drying period (72 h). A 3 percent Tide solution in water is prepared. The specimens are dipped into the solution without touching the wall or bottom of the beaker. After 72 h the specimens are removed, rinsed under a gentle stream of water, allowed to dry for 30 min and examined for whittening, blistering or removal of film. The test may be continued for a week (168 h), if necessary.

Finally, toxicity tests may be administered on nail enamels in accordance with the Federal Hazardous Substances Act Regulations. Acute Oral Toxicity (Rat), Primary Dermal Irritation (Rabbit), Acute Dermal Toxicity (Rabbit), Skin Sensitization (Guinea Pig), and Draize Ocular Irritation (Rabbit) are common for nail enamels. Human use tests involving 50–100 subjects may also be employed to determine if the product is an irritant or sensitizer.

CONCLUSIONS

Nail enamels should be easy to apply and should dry and harden rapidly. They should be waterproof, well adherent, glossy, elastic, resistant to chipping and abrasion. Lastly, lacquers must be non-toxic, non-irritating and non-sensitizing to the skin. The behavior of nail enamel on a substrate provides a good indication of its behavior on finger nails but it is still necessary to study the product by actual application to the nails. Again tests are made on parameters such as flow, evenness of application, drag on the applicator brush, smoothness of the dried film, hardness, gloss and wear resistance. Ultimately, all of the aforementioned must be evaluated on nails. Nail enamels must be carefully tested to make sure that they meet the performance specifications which have been set up by both marketing and technical executives. The judicial selection of testing methods and the correct interpretation of data are vitally important to the development of improved nail coating formulations. The performance of a nail enamel and its components is of primary concern to the lacquer chemist, he must prescribe the tests, interpret and redefine the data while recognizing their overall significance, and apply conclusions based on the information obtained in the tests.

REFERENCES

(1) Peter Diamandis, Eye, Lip and Nail Care, *Product Marketing,* p. S60-62 (Special Issue, Winter 1980).
(2) H. J. Wing in *The Chemistry And Manufacture Of Cosmetics,* Volume IV, 2nd ed., M. G. deNavarre, Ed., (Continental Press, Orlando, FL, 1975), pp 1001-1002.
(3) A. Shansky, Establishing physical parameters of nail lacquers, *Drug & Cosmetics Industries,* **123** (5), 48 (1978).
(4) M. Schlossman, Modern nail enamel technology, *J. Soc. Cosmet. Chem.,* **31**, 29-36 (1980).
(5) F. W. Busch, Jr. and M. G. Brookins, "Thixotropic Flow in Cosmetics: Utility and Evaluation," presented at the New England Chapter of the Society of Cosmetic Chemists, Boston, April 25, 1974.