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Patent Section, Lab.
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Marshall Laboratory
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MEMORANDUM REPORT NO. M-716

PREPARED BY: JAMES T. HARRIS, JR.

CUSTOMER'S USE OF INFRARED SPECTROSCOPY TO DETECT CHANGES IN PAINT FORMULATIONS (MICHIGAN STATE HIGHWAY DEPARTMENT)

Introduction:

Two members of the Chemical Research Section of the Michigan State Highway Department recently visited this laboratory to discuss the application of infrared spectroscopy to measurements of variations in paint composition: Mr. C. C. Rhodes, head of the section, and Mr. Paul Biefeld, infrared spectroscopist. Their visit was arranged by Mr. E. A. Finney, Assistant Testing and Research Engineer of the Highway Department who initially contacted R. E. Pike at Flint.

The Highway Department receives sample paints for field testing on roads, bridges, signs, etc. one year and then purchases the particular paints selected from these tests for use the following year. They purchased more than a quarter of a million dollars worth of paint this past spring on the sole condition that this paint would be the same as the paint tested in 1953 and that it would equal that paint in performance. Infrared spectroscopy is being used to see that the original paint formulations of 1953 have not been changed in 1954.

Summary:

At least one large-scale paint consumer is now using three infrared spectra on the solvent, pigment and binder fractions to signify the formula specifications for the purchased paint. This is a new development in the paint field, but other industries have previously made extensive use of infrared specifications. These three standard infrared spectra will stop a paint manufacturer from submitting a high-grade paint for initial testing and then actually shipping a low-grade paint for use when his product is purchased.

At present only the larger paint manufacturers utilize infrared spectroscopy in their research, development and production activities. Knowing the great benefits derived from our own use of this technique, it is very probable that it may become a standard method of paint analysis throughout the industry in future years. Some of the advantages and disadvantages that the du Pont Company would encounter if this technique becomes widely employed are summarized.

Discussion:

Prior to the Highway Department's contact with the Marshall Laboratory, some initial infrared work on paints had been accomplished with a Beckman spectrophotometer by Mr. Biefeld who previously did infrared research at Michigan State College. These initial results looked so promising that the Department will most probably purchase a $14,000 Perkin-Elmer double-beam spectrophotometer. With this well-trained spectroscopist and an excellent instrument, this highway department will be well equipped to accomplish routine infrared analysis on paints as well as asphalts and other roadbuilding materials.

The Highway Department will receive samples of paint for field testing this year. The usual physical tests will also be performed: viscosity, drying time, weight per gallon, tristimulus color values, etc. On the basis of the field test results, paints having the best performance at lowest cost will be selected for purchase and use next year for specific purposes. After particular paints have been selected, three infrared spectra will be recorded on the solvent, binder and pigment components. These three spectra for each paint type will then serve as standard spectra which will signify the formula specifications.

Next year when large volumes of paint will be purchased for use, a sample from each batch will be tested by the standard physical tests and especially by the three infrared spectra of the paint components. These spectra will be compared with the standard spectra of the original sample recorded the previous year. If changes have been made in the formulation, the two spectra will be different in the majority of cases. (Changes of the order of 1% composition will generally remain undetected.)

1. The two solvent spectra will be different if one sample contains more and/or a different type of aromatic hydrocarbon (ester, ketone or alcohol) than the other.

2. Pigment spectra will be different if $CaCO_3$ is used to replace $BaSO_4$ or chrome yellow in place of toluidine yellow.

3. Resin spectra will be different if an alkyd resin is substituted for an alkyd-UF blend.

Such changes in paint formulation will thus be readily detected by these three 20-minute infrared spectra. When this occurs the paint supplier will be contacted, and a decision to reject or accept the batch will then be made. In most cases the "off-standard" batch will be rejected because the paint delivered is not the same as the paint originally tested.

Minor changes can be made by a manufacturer in pigment composition (alteration of TiO_2/silicate ratio) or in solvent composition (alteration of ketone/ester ratio) without adding new components to the original formula. Such minor changes would also be detectable by the infrared technique. When the Highway Department detects such changes, the following question must be answered before a decision to reject or accept a batch can be made: How much spectral variation between batch samples and the standard paint formulation should be allowed before it is found that the paints have significant composition and/or performance differences?

This question was discussed at length by the visitors and the writer, and no clear answer could be found. A definite percentage spectral variation of 0.5%, 1% or 5% cannot be set for all types of materials. In many cases rather large variations in solvent composition can be allowed with small paint performance changes, and here the allowed spectral variation could be large. In other instances solvent composition may be confined to very narrow limits, and here spectral variations would have to be small. The result of the discussion was that the Highway Department would have to correlate spectral variations with performance and from this data specify to the supplier the allowable spectral variations for various types of paints.

The above paragraphs have described how changes in paint formulation can readily be detected in most instances by infrared spectroscopy. This method of paint analysis has been employed in the Marshall Laboratory for many years, and it is known that some other paint manufacturers, Sherwin-Williams, for example, have excellent infrared equipment. Many solvent and resin suppliers extensively use infrared techniques to check the composition of their products. Now it is known that at least one customer is routinely checking the constancy of paint formulations by this technique. This is very significant, since it is the first time that the writer has known a customer to use this technique on paint which he has purchased.

Since this customer will tell all of its suppliers how their paint is being tested, other paint manufacturers may thus be forced into buying infrared equipment for use as a test method. For example, the Glidden Company is extremely interested and also worried about this infrared technique because this company has not had previous experience with infrared methods of analysis. Other customers will soon hear about this rapid method, and it is probable that in the future many large-volume purchasers of paint will adopt this test method for formulations, especially those who already have infrared equipment for other uses. This would not be unusual, since a variety of industries have made use of infrared "specification" spectra during the past few years. Very recently the cosmetic industry has used infrared specifications for aromatic oils to prevent unauthorized addition of non-aromatic or inert ingredients.

During the past few weeks the writer has talked with several chemists and supervisors about our customers' use of infrared spectroscopy. Special emphasis was placed on the advantages and disadvantages that the du Pont Company would encounter if this test method became widely employed. These will be briefly summarized.

ADVANTAGES

1. This rapid method of analysis will stop sub-standard paint manufacturers from submitting a high-grade paint for testing and then actually shipping a low-grade paint for use when his product is purchased at a later date.

2. This infrared technique could be used as one selling point for du Pont paint, since it would show our customers how du Pont uses the most modern scientific instruments to check the constancy of our formulations. (For variable formulations, this could not be done.) We have this advantage over most of our competitors at present, but this condition would not prevail for long if many other paint manufacturers started extensive use of infrared methods.

3. Complaints about the performance of du Pont paints sometime arise when a customer mixes du Pont paint with other paints or additives. When such complaints are sent to the Analytical Section the use of infrared spectroscopy is the first step in the chemical analysis of the "off-standard" sample. If customers who make these mixtures knew that we can rapidly detect unauthorized additives in our paint, possibly some of these complaints could be avoided.

DISADVANTAGES

1. A customer might make his formula specifications too rigid by requiring exact duplication of his standard infrared spectra. This difficulty can be overcome by an agreement between supplier and purchaser regarding the allowable variations in spectra and compositions.

2. Customers would have to be informed immediately after an older product had been reformulated, but it would not be necessary to tell exactly what the new formula is. Those who had standard spectra of the older product would easily detect this formula change since the spectra of the new product would be different from the old in many cases.

3. Many of du Pont's competitors, who do not now use rapid infrared methods to break down new du Pont formulations, would have the use of this rapid method of paint analysis in the future if this technique becomes extensively employed in the paint industry.

4. Production costs would increase somewhat since control labs would have to purchase infrared instruments and record spectra of components of paint batches as specification tests before shipment. Some customers may want standard spectra sent to them when they purchase large amounts of a particular paint. (Carbide and Carbon has standard spectra available on commercial chemicals and solvents that it sells.)

James T. Harris Jr.

JAMES T. HARRIS, JR.

JTH:eaw
Attachment
7/16/54

Appendix:

INFRARED AND VISIBLE SPECTROSCOPY

For readers of this report not familiar with infrared spectroscopy, a brief comparison of visible spectroscopy with infrared is made. The color of a paint film can be ascertained from its reflectance spectrum recorded on a visible spectrophotometer (0.4-0.7 micron). The shape of the spectral curve tells whether the paint film is blue, green, yellow or red; but only limited information is obtained about the chemical structures of the pigments and no information is obtained regarding the resin types. Using a different instrument and technique, infrared spectroscopy (2-15.5 microns) allows the particular chemical structures of the pigments to be determined but gives no information about color. The infrared spectrum serves as a "fingerprint" to characterize a particular chemical structure; and thus TiO_2, $BaSO_4$, silica and Toluidine Red can each be rapidly detected in a mixture without using separation procedures. In a similar way infrared spectroscopy characterizes by "fingerprint" spectra the various components of solvents (aliphatic and aromatic hydrocarbons, esters, ketones, alcohols, etc.) and of resins (melamine, alkyd, UF-melamine mixture, etc.). In addition to these qualitative identifications of paint components, infrared techniques can be used quantiatively in many instances.

JTH:eaw
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