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MISSOURI COOPERATIVE HIGHWAY RESEARCH PROGRAM
REPORT 71-4A

INVESTIGATION OF PAINTS AND GLASS BEADS USED IN TRAFFIC DELINEATION MARKINGS

ADDENDUM TO PHASE 2 REPORT

MISSOURI STATE HIGHWAY DEPARTMENT
FEDERAL HIGHWAY ADMINISTRATION

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INVESTIGATION OF PAINTS AND GLASS BEADS USED IN TRAFFIC DELINEATION MARKINGS ADDENDUM TO PHASE 2 REPORT EVALUATION OF HIGH HEAT TRAFFIC DELINEATION PAINTS UNDER FIELD CONDITIONS

STUDY 69-6

Prepared by

MISSOURI STATE HIGHWAY DEPARTMENT

Division of Materials and Research

and

Division of Maintenance and Traffic

December 1972

in cooperation with

U. S. DEPARTMENT OF TRANSPORTATION

Federal Highway Administration

The opinions, findings, and conclusions expressed in this publication are not necessarily those of the Federal Highway Administration.

SYNOPSIS

This addendum contains additional chemical information on the proprietary high heat paints of the Phase 2 Report. Tests include the infrared spectra for the vehicle and solvent portion of the paint and an Ortec non-dispersive X-ray spectrometer and an ARL microprobe to determine the properties of the pigment portion of the paint.

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INTRODUCTION

The Phase 2 Report of the Investigation of Paints and Glass Beads Used in Traffic Delineation Markings incorporated five high heat proprietary type paints. Each paint was applied in two colors, white and yellow. The evaluation was confined to the application of paint stripes four inches wide placed transverse to the direction of travel on asphaltic concrete and concrete surfaces. These paints were field evaluated by visual ratings of general appearance and field condition, inclusive of abrasion and chipping.

The manufacturers of these proprietary products were very reluctant to divulge the composition of their trade products, therefore, the infrared spectral curves on the separated pigment, vehicle, and solvent were obtained for each paint to determine its generic composition. The Missouri State Highway Department contracted the work to the Materials Research Center, University of Missouri-Rolla. The work consisted of qualitative identification by chemical components of the pigments and vehicle constituents using a combination of Infrared Spectral Curves, X-ray and Nuclear Magnetic Resonance.

Evaluation of each paint was conducted by using a Beckman IR-12 spectrophotometer for the infrared spectra for the vehicle and solvent portion. It was concluded that an Ortec non-dispersive X-ray spectrometer and an ARL microprobe would be better suited to determine the properties of the pigment portion of the paint.

The procedures, spectrograms and chemical components of each paint are included for informational value.

PROCEDURES FOR DETERMINATION OF GENERIC COMPOSITIONS

Ten paint samples were qualitatively analyzed to determine the generic compositions of vehicles, solvents and pigments. The following procedures were used for the analysis of these paints:

Vehicles:

In the cases where the pigments had settled, a sample of the vehicles and solvent was applied to a KBr plate and dried in a 120°C oven for 5-10 minutes. Paints in which the pigments had not settled were diluted with a mixture of equal parts of xylenes, methyl ethyl ketone, and methylene chloride. The diluted mixture was centrifuged to settle the solids. The solvent was evaporated on a KBr plate to leave a film of the vehicle itself. Infrared spectra were obtained using a Beckman IR-12 spectrophotometer.

Solvents:

The solvents were removed from the paint by simple distillation. Where possible, individual solvents were separated before infrared analysis; otherwise, a composite spectrum was obtained. Infrared spectra of all solvents were obtained using KBr liquid cells on a Beckman IR-12. This technique proved more meaningful than NMR or chromatographic techniques.

Pigments:

A sample of each paint was diluted with a mixture of equal parts of xylene, methyl ethyl ketone, and methylene chloride. The diluted mixture was centrifuged and the solvent decanted. More of the mixed solvent was added to the solids, the mixture thoroughly stirred, centrifuged, and decanted as before. The washing procedure was repeated twice more. The solids were dried in a 120°C oven for 10 minutes and analyzed by an Ortec non-dispersive X-ray spectrometer and by an ARL microprobe.

Spectrophotometer Settings and Constants:

SB = 98 SB/DB Energy Ratio = 1
DB = 98 Resolution = Maximum

Speed = 200
Gain = 350
Period = 2
Ordinate Seale = 0 - 100

RESULTS OF TESTS

The paint samples were tested by obtaining one IR spectrogram for the separated vehicle and solvent portions. The one exception was paint Type I where it was necessary to test the components of the solvent portion separately. The spectrogram obtained from single samples are shown in Figures 1 through 12, pages 6 through 17. The results of these determinations are shown in Table 1, page 5.

The following comments refer to the analyses of the data:

1. The infrared spectra of all the paints except Type O yellow and white paints revealed that the vehicles were all modified phthalic alkyds. The statements concerning "short", "medium", or "long" are based on comparison with known alkyds and are considered to be more probable designations.

2. The non-dispersive X-ray and microprobe analyses confirmed the inorganic elements present as pigments.

The major and minor components of the pigments are transcribed into the most probable chemical compounds (some of the minor components could be due to residues of driers in the washed pigments) and are as follows:

Paint Type G, Yellow, Laboratory Number 70-12890; Silica, lead chromate, calcium (~ calcium sulfate as an extender), aluminum oxide, trace of iron compounds could be an impurity in the other pigments or could come from mixing tanks or storage containers.

Paint Type G, White, Laboratory Number 70-12891; Titanium dioxide + calcium sulfate.

Paint Type I, Yellow, Laboratory Number 70-12892; Lead chromate, silica, calcium carbonate.

Paint Type I, White, Laboratory Number 70-12893; Titanium dioxide + calcium sulfate, calcium carbonate, silica.

Paint Type K, Yellow, Laboratory Number 70-12894; Lead chromate, calcium carbonate, silica, zinc oxide.

Paint Type K, White, Laboratory Number 70-12895; Calcium carbonate, titanium dioxide + calcium sulfate, zinc oxide, aluminum oxide.

Paint Type M, Yellow, Laboratory Number 70-12896; Lead chromate, calcium carbonate, silica.

Paint Type M, White, Laboratory Number 70-12897; Calcium carbonate, silica.

Paint Type O, Yellow, Laboratory Number 70-12898; Lead chromate, calcium sulfate, silica, aluminum oxide.

Paint Type O, White, Laboratory Number 70-12899; Calcium sulfate, titanium dioxide, silica.

3. The paint from sample cans identified as Laboratory Numbers 70-12898 and 70-12899 were solidified in their containers. Portions of these samples were extracted using different solvent mixtures. Both samples showed an oil modified polyamide as a primary constituent. This did not preclude the possibility that other materials (crosslinked in the can) were present and were not extracted.

Table 1

Generic Compositions of High Heat Paints

Vehicle	Solvents	Pigments: Major Components	Pigments: Minor Components
Paint Type G, Yellow, 70-12890			
Oil Modified Phthalic Alkyd, Short-Med. Oil	Trichloroethylene Comm. Mineral Spirits	Si, Pb, Ca, Cr	Al, Fe
Paint Type G, White, 70-12891			
Oil Modified Phthalic Alkyd, Med.-Long Oil	Trichloroethylene, Comm. Mineral Spirits	Ti, Ca	Al, Si
Paint Type I, Yellow, 70-12892			
Oil Modified Phthalic Alkyd, Med.-Long Oil	Methylene Chloride, Comm. Mineral Spirits	Pb, Ca, Cr, Al, Si	Fe
Paint Type I, White, 70-12893			
Oil Modified Phthalic Alkyd, Med.-Long Oil	Methylene Chloride, Comm. Mineral Spirits	Ca, Ti, Si	Al, Fe
Paint Type K, Yellow, 70-12894			
Oil Modified Phthalic Alkyd, Med.-Long Oil	Trichloroethylene	Ca, Pb, Cr	Si, Zn Fe
Paint Type K, White, 70-12895			
Oil Modified Phthalic Alkyd, Med.-Long Oil	Trichloroethylene	Ca, Ti, Si, Zn	Fe, Cr, Al
Paint Type M, Yellow, 70-12896			
Oil Modified Phthalic Alkyd, Short-Med. Oil	Toluene, Xylenes	Ca, Si, Pb, Cr	
Paint Type M, White, 70-12897			
Oil Modified Phthalic Alkyd, Med.-Long Oil	Toluene, Xylenes	Ca, Si	Ti, Cr Fe
Paint Type O, Yellow, 70-12898			
Oil Modified Polyamide	Toluene	Ca, Pb, Cr, Si	Al, Fe
Paint Type O, White, 70-12899			
Oil Modified Polyamide	Toluene	Ca, Ti	Si, Al, Cr, Fe

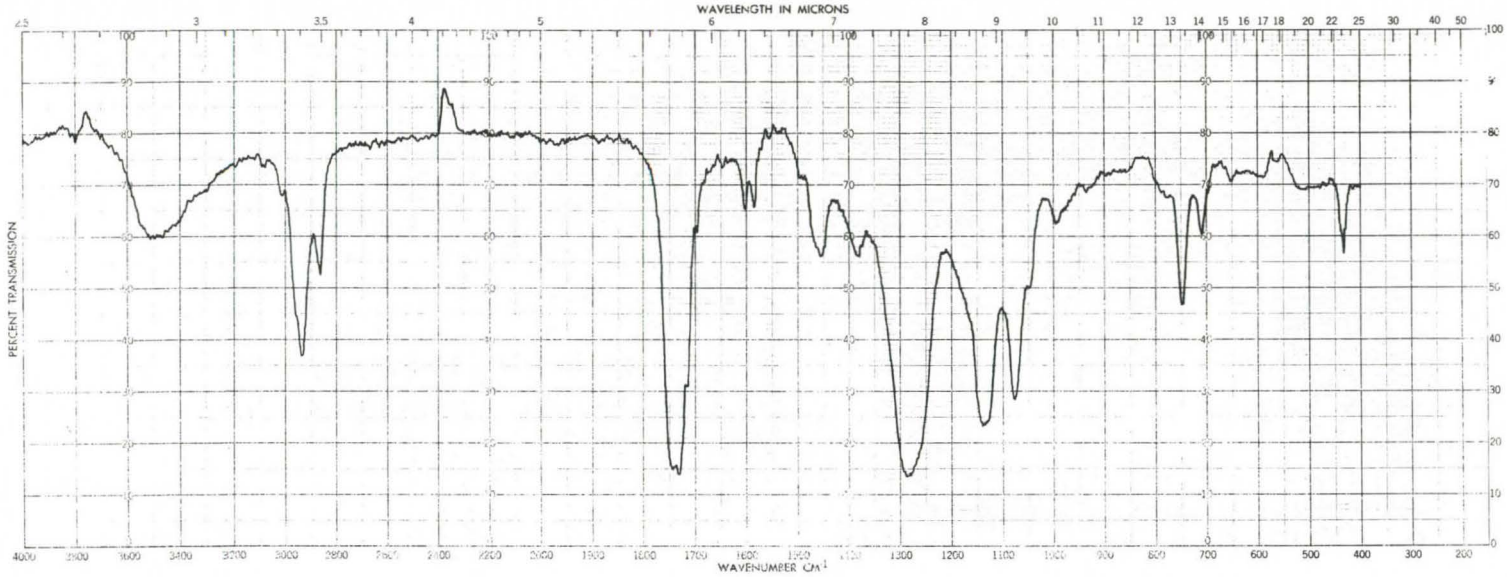


FIGURE 1

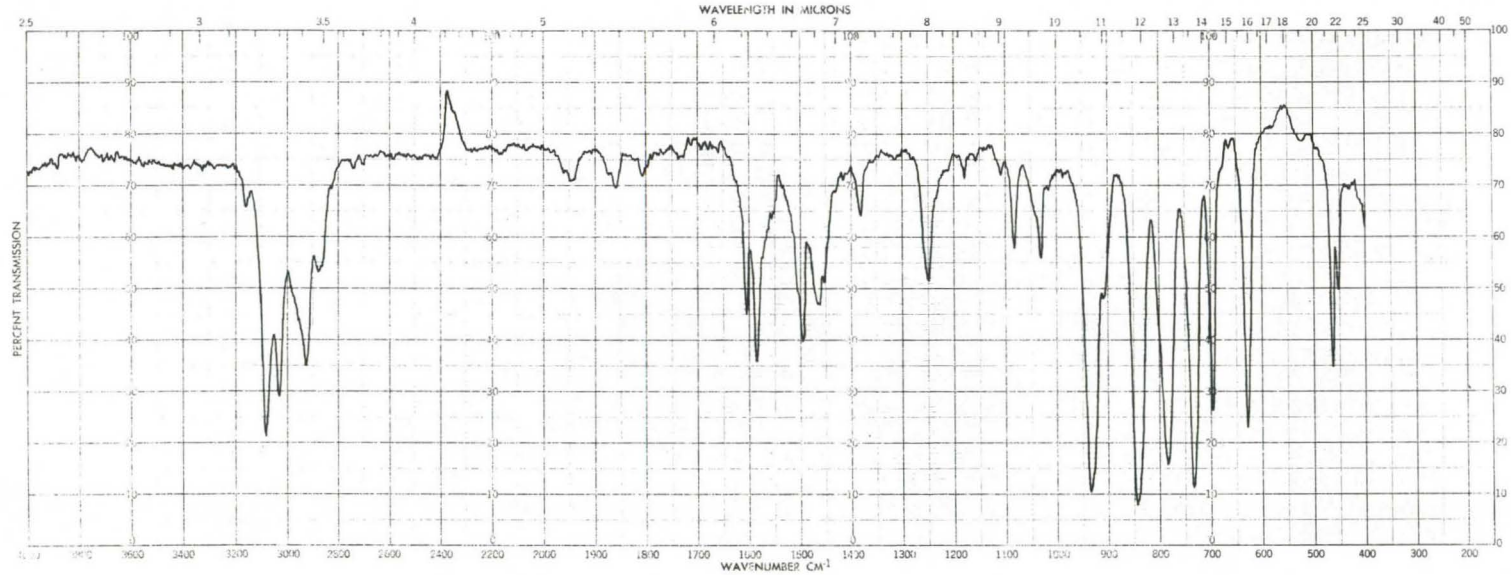
PAINT TYPE - G

(VEHICLE)

COLOR - YELLOW
LAB NO 70-12890

GENERIC COMPOSITION:

OIL MODIFIED
PHTHALIC ALKYD,
SHORT-MED. OIL



PAINT TYPE - G

(SOLVENTS)

COLOR - YELLOW
LAB NO 70-12890

GENERIC COMPOSITION:

TRICHLOROETHYLENE
COMM. MINERAL SPIRITS

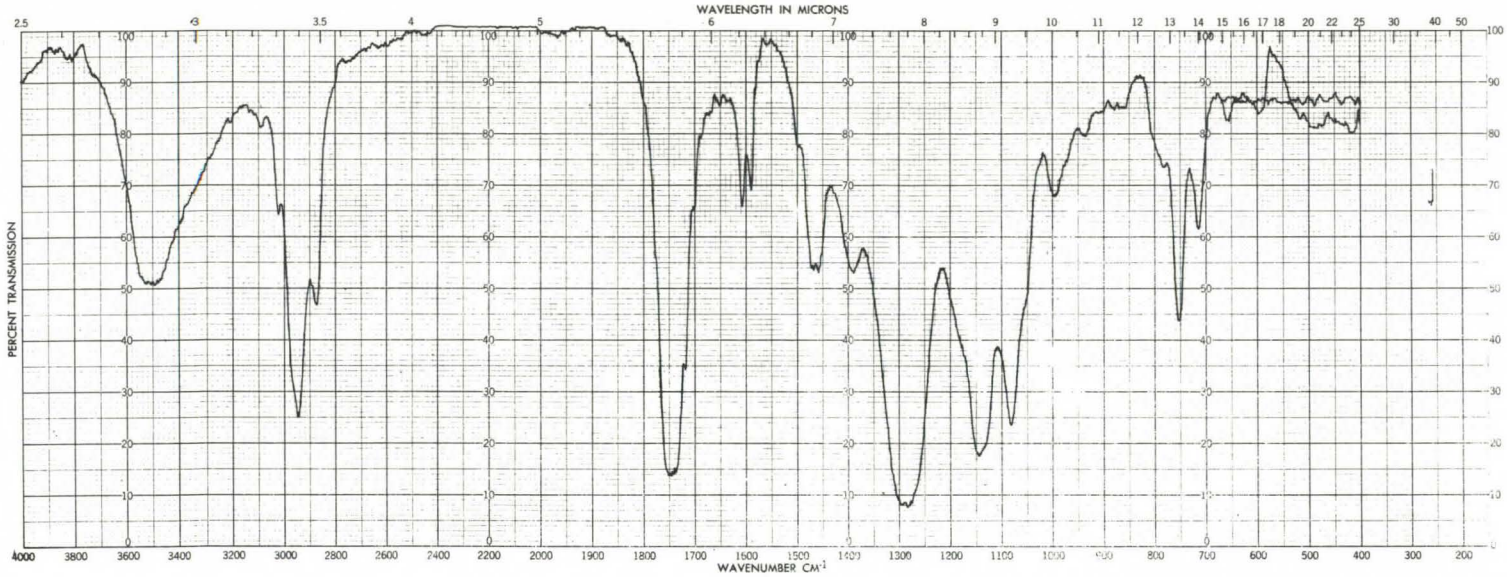


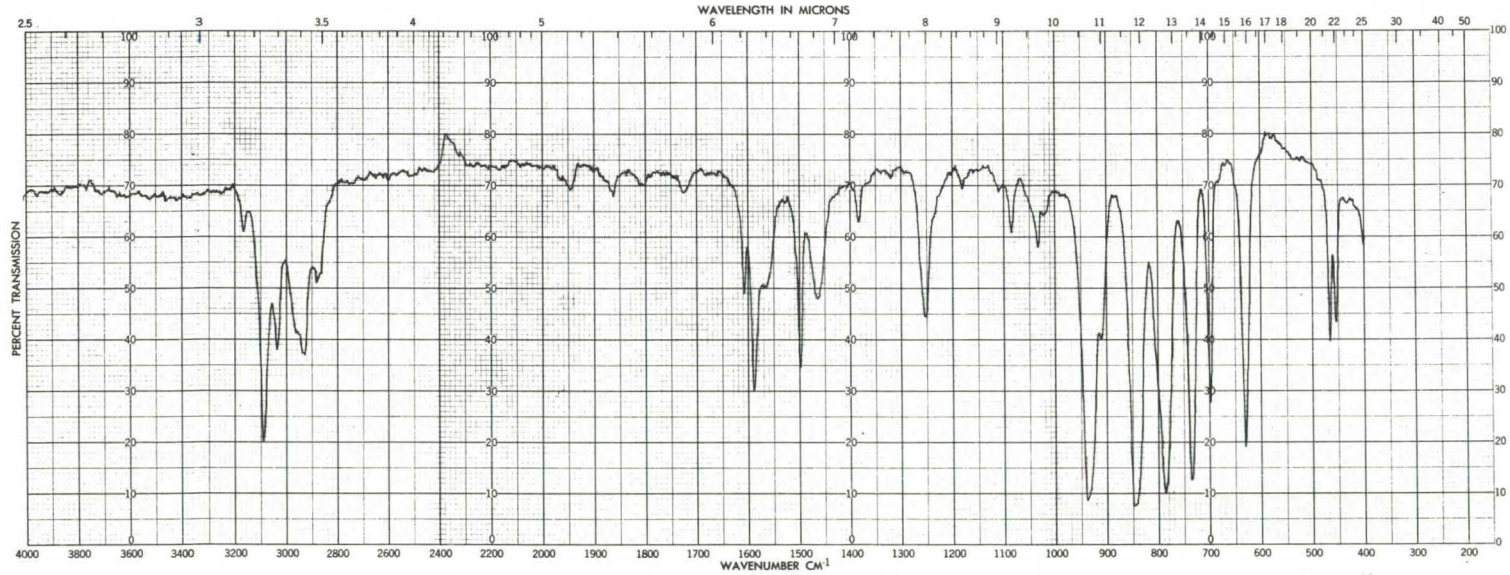
FIGURE 2

PAINT TYPE - G

(VEHICLE)

COLOR - WHITE
LAB NO 70-12891

GENERIC COMPOSITION:
OIL MODIFIED
PHTHALIC ALKYD,
MED.-LONG OIL



PAINT TYPE - G

(SOLVENTS)

COLOR - WHITE
LAB NO 70-12891

GENERIC COMPOSITION:
TRICHLOROETHYLENE
COMM. MINERAL SPIRITS

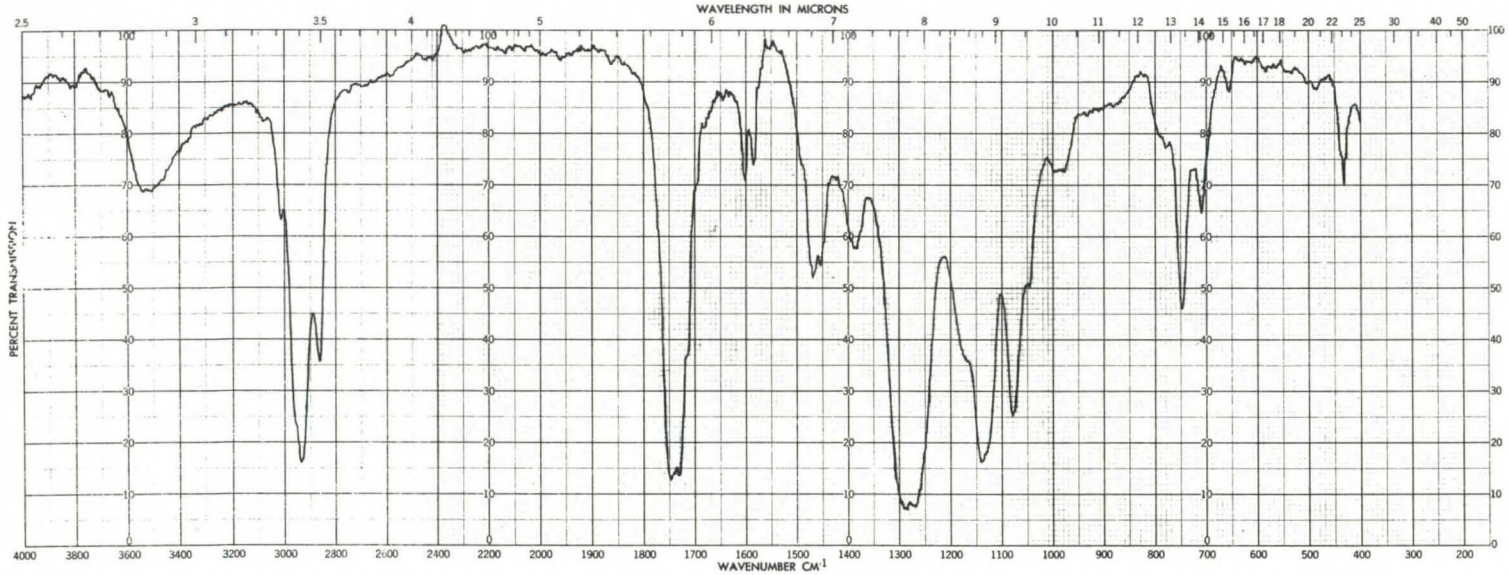


FIGURE 3

PAINT TYPE - I

(VEHICLE)

COLOR - YELLOW
LAB NO 70-12892

GENERIC COMPOSITION:

OIL MODIFIED PHTHALIC ALKYD, MED.-LONG OIL

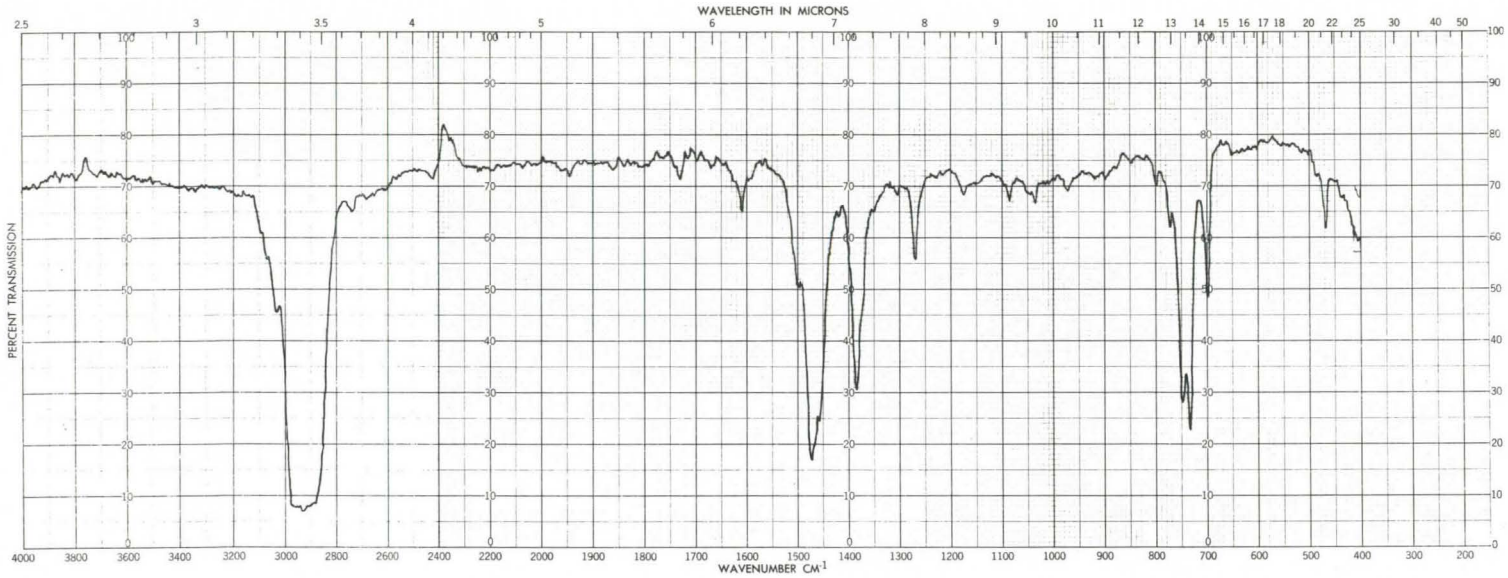


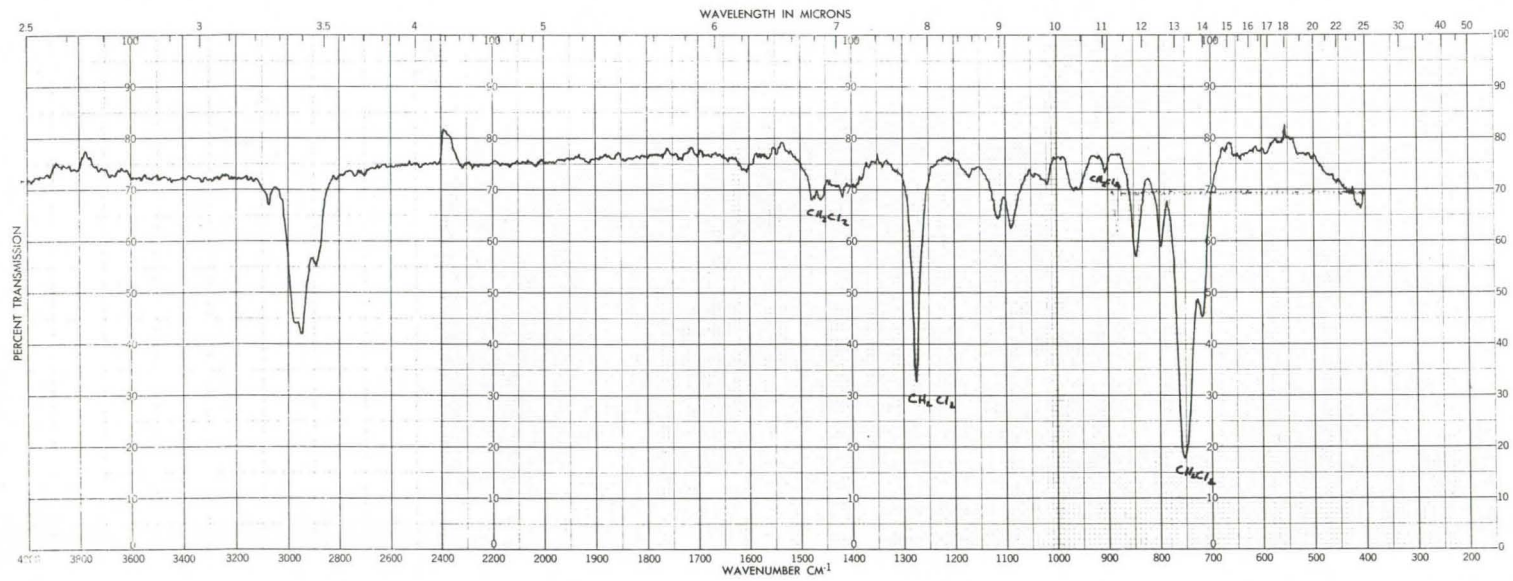
FIGURE 4

PAINT TYPE - I

(SOLVENTS)

COLOR - YELLOW
LAB NO 70-12892

GENERIC COMPOSITION:
COMM. MINERAL SPIRITS



PAINT TYPE - I

(SOLVENTS)

COLOR - YELLOW
LAB NO 70-12892

GENERIC COMPOSITION:
METHYLENE CHLORIDE

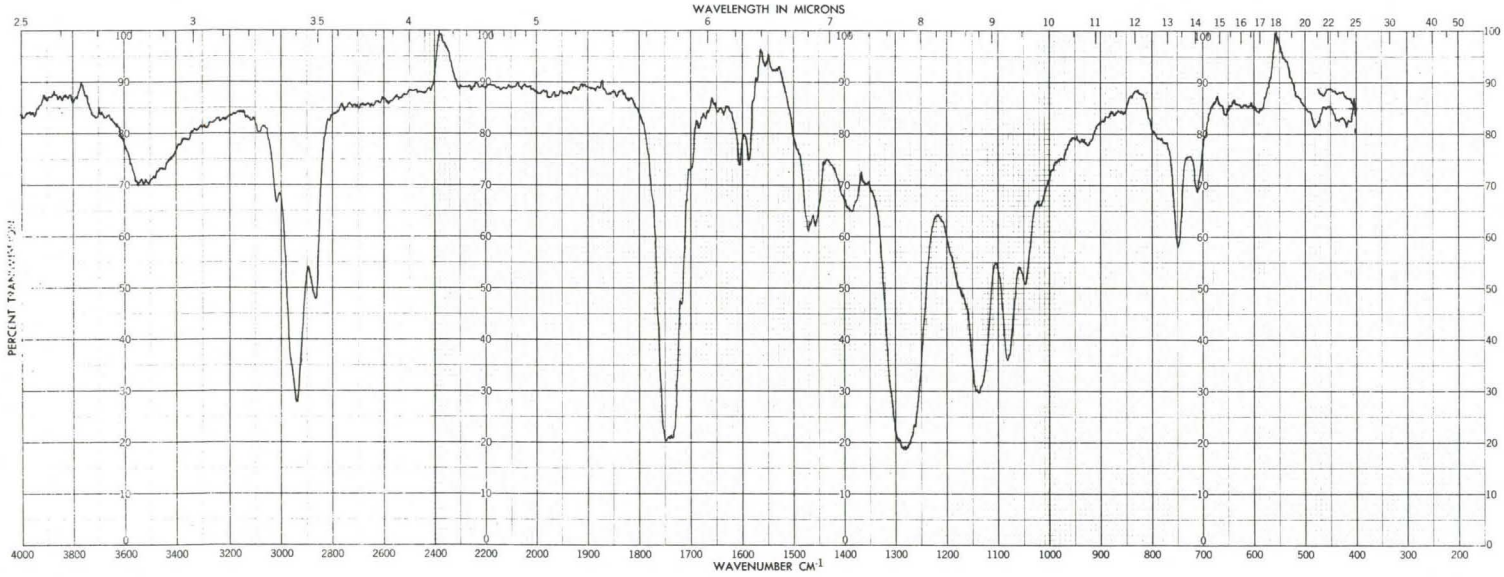


FIGURE 5

PAINT TYPE - I

(VEHICLE)

COLOR - WHITE
LAB NO 70-12893

GENERIC COMPOSITION:

OIL MODIFIED PHTHALIC ALKYD, MED.-LONG OIL

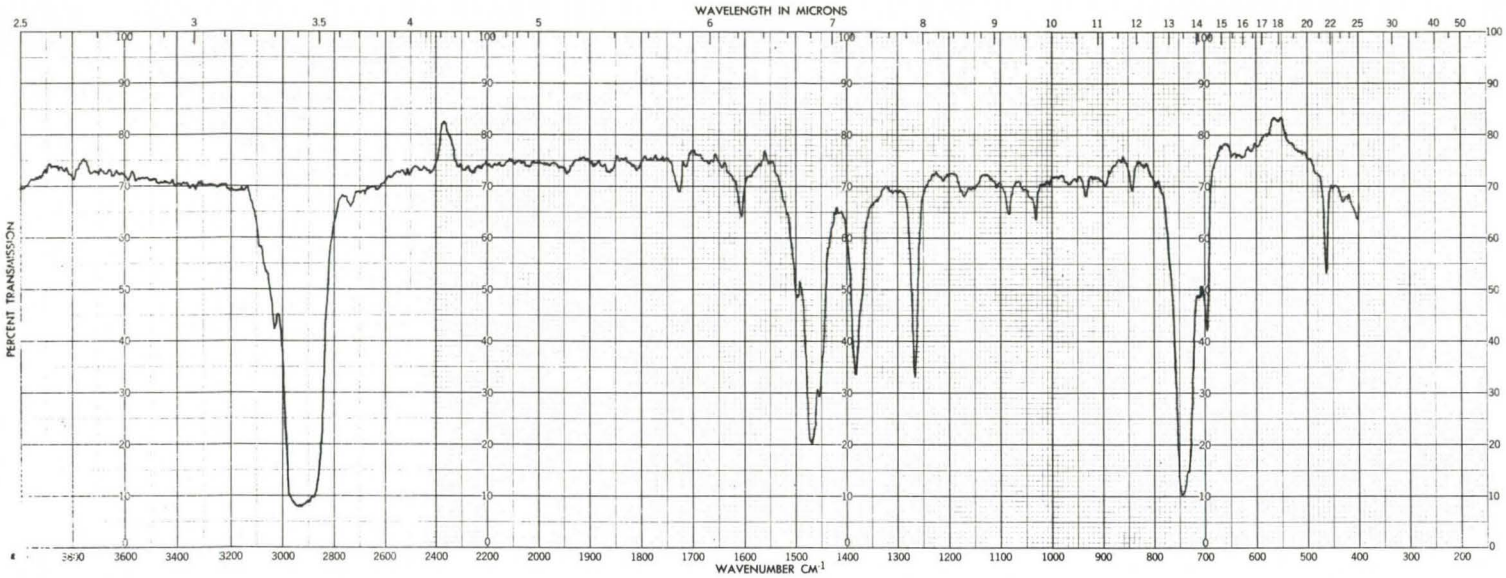


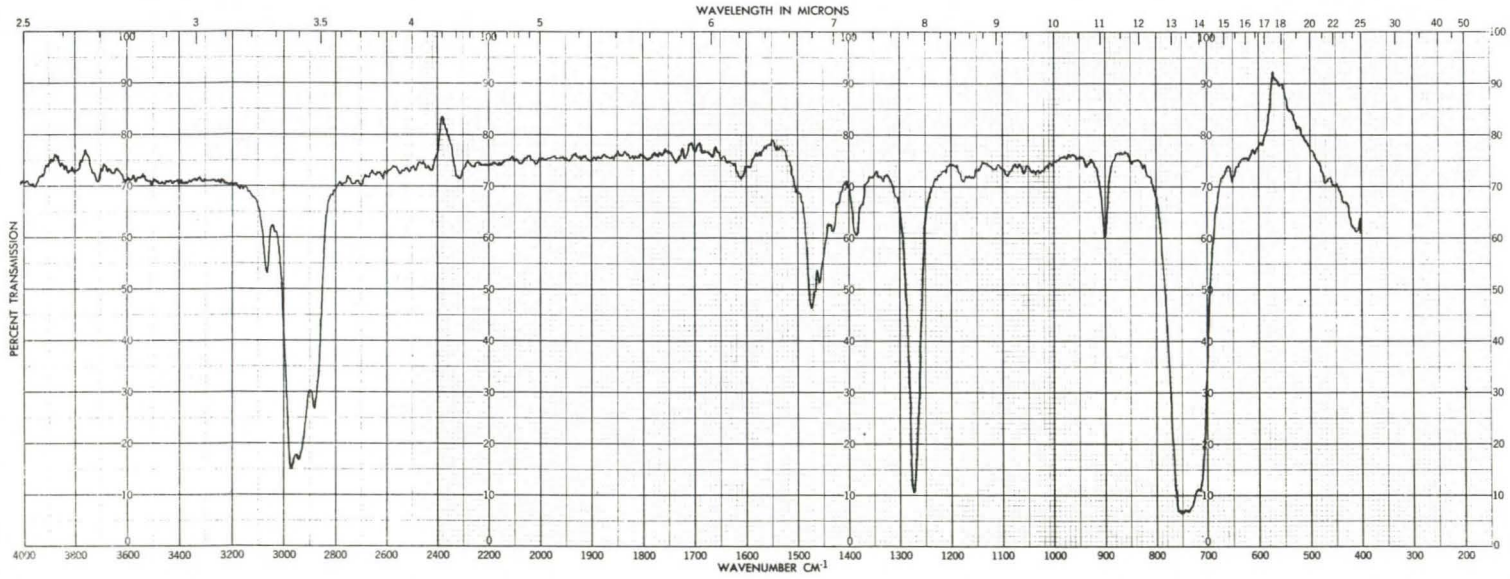
FIGURE 6

PAINT TYPE - I

(SOLVENTS)

COLOR - WHITE
LAB NO 70-12893

GENERIC COMPOSITION:
COMM. MINERAL SPIRITS



PAINT TYPE - I

(SOLVENTS)

COLOR - WHITE
LAB NO 70-12893

GENERIC COMPOSITION:
METHYLENE CHLORIDE

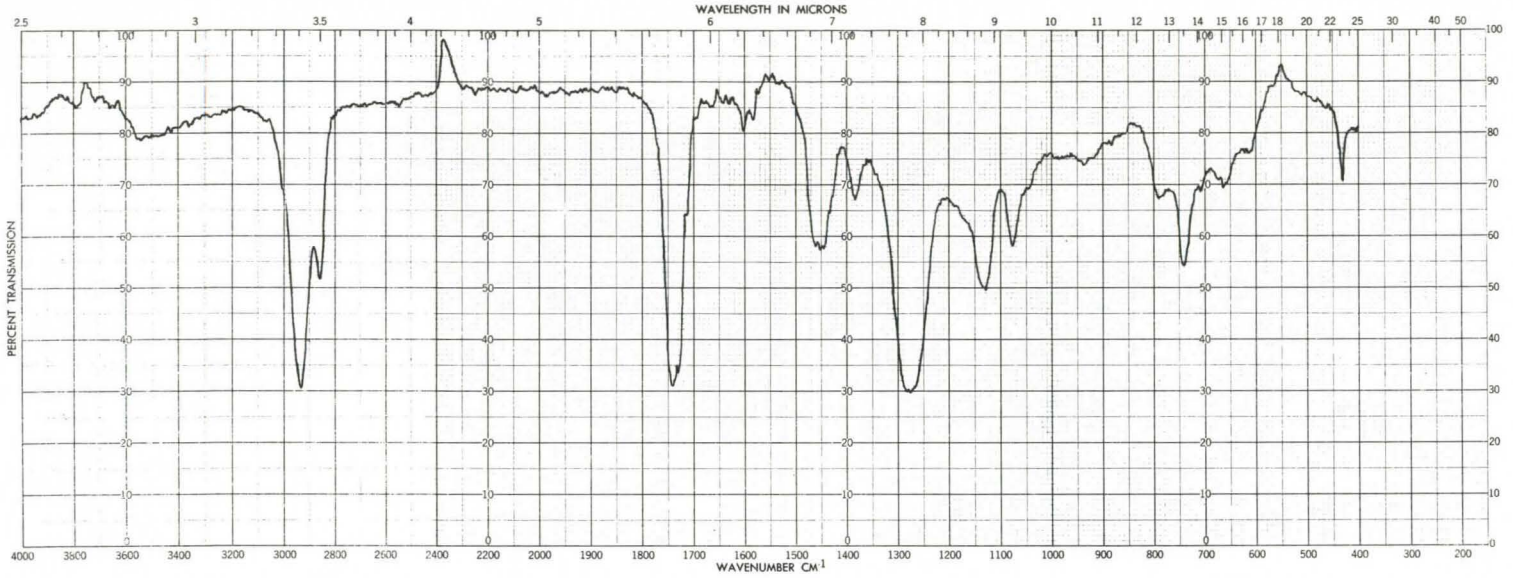


FIGURE 7

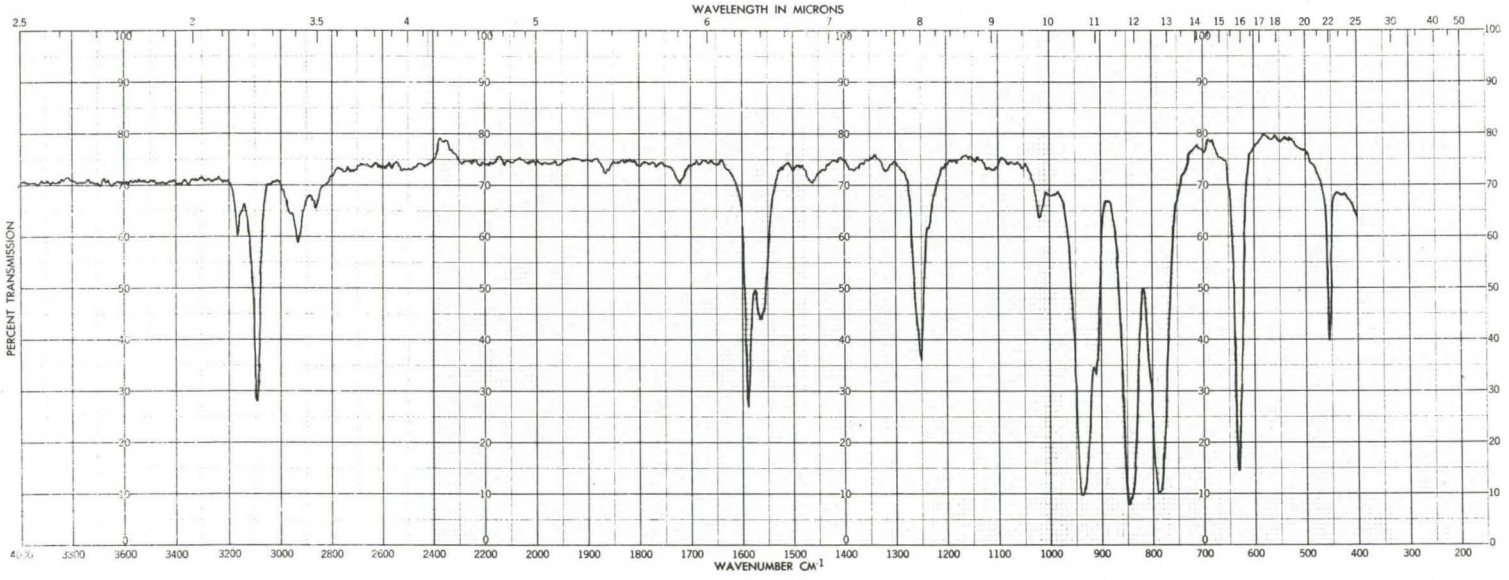
PAINT TYPE - K

(VEHICLE)

COLOR - YELLOW
LAB NO 70-12894

GENERIC COMPOSITION:

OIL MODIFIED PHTHALIC ALKYD, MED.-LONG OIL



PAINT TYPE - K

(SOLVENTS)

COLOR - YELLOW
LAB NO 70-12894

GENERIC COMPOSITION:

TRICHLOROETHYLENE

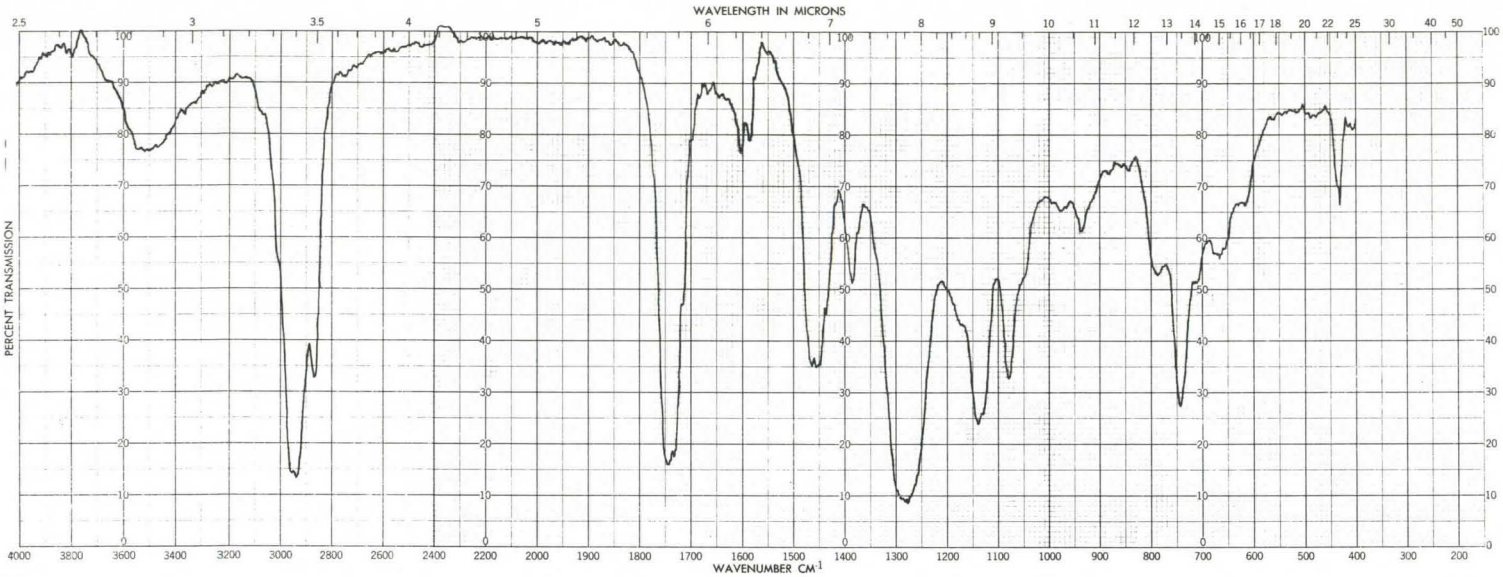


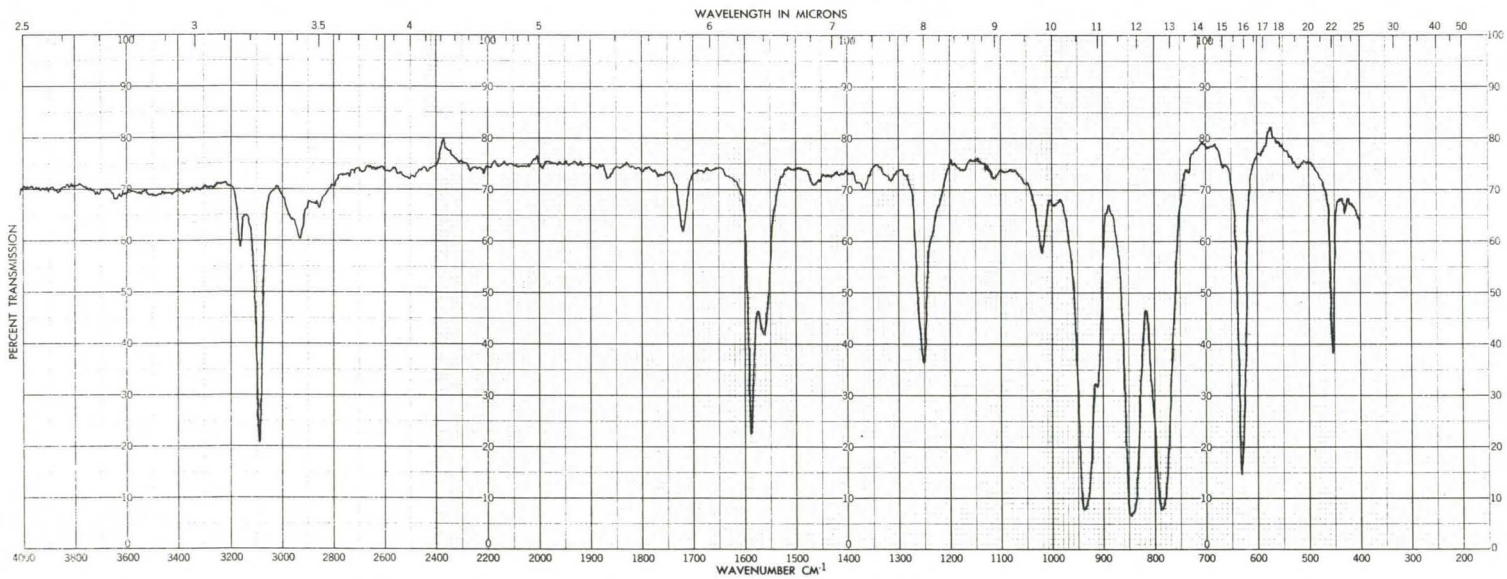
FIGURE 8

PAINT TYPE - K

(VEHICLE)

COLOR - WHITE
LAB NO 70-12895

GENERIC COMPOSITION:
OIL MODIFIED PHTHALIC ALKYD, MED.-LONG OIL



PAINT TYPE - K

(SOLVENTS)

COLOR - WHITE
LAB NO 70-12895

GENERIC COMPOSITION:
TRICHLOROETHYLENE

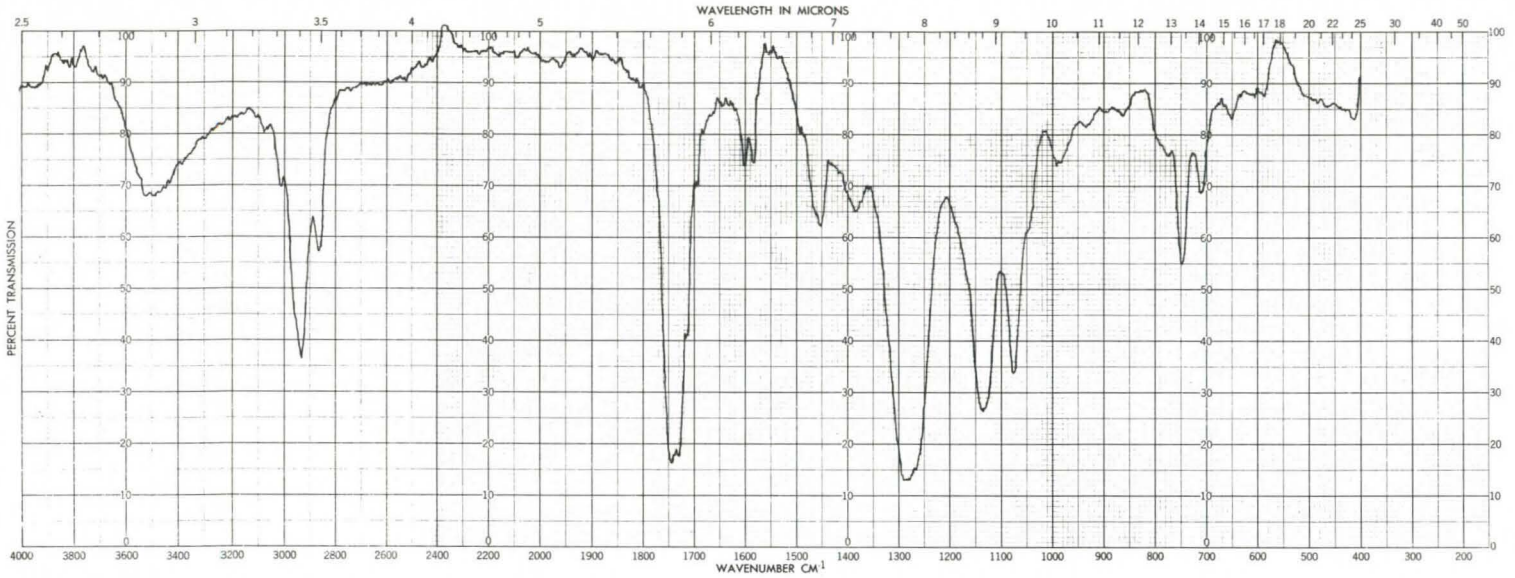


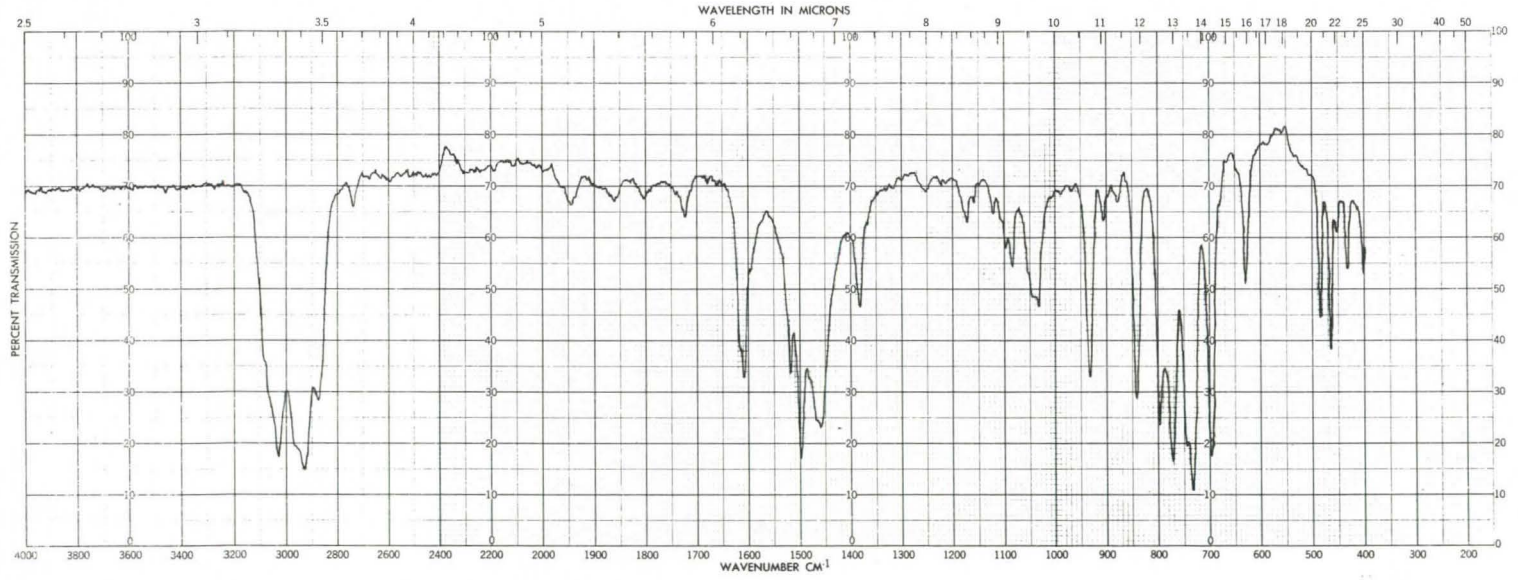
FIGURE 9

PAINT TYPE - M

(VEHICLE)

COLOR - YELLOW
LAB NO 70-12896

GENERIC COMPOSITION
OIL MODIFIED PHTHALIC ALKYD, SHORT - MED. OIL



PAINT TYPE - M

(SOLVENTS)

COLOR - YELLOW
LAB NO 70-12896

GENERIC COMPOSITION
TOLUENE & XYLENES

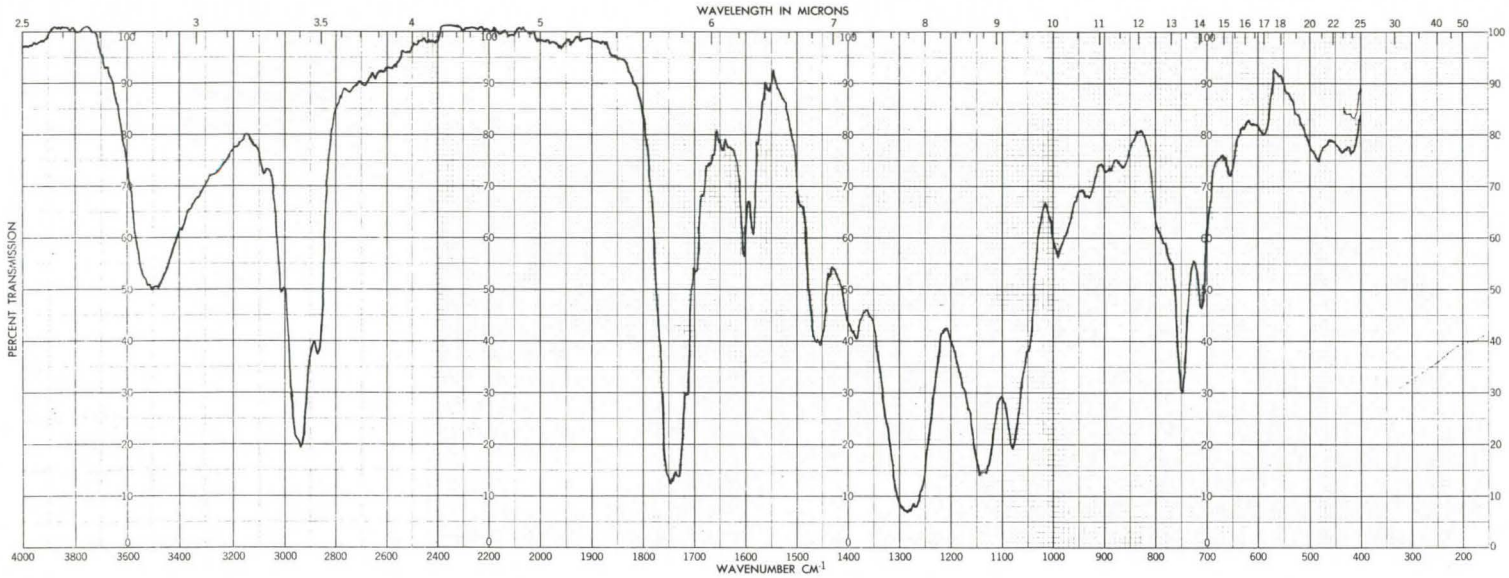


FIGURE 10

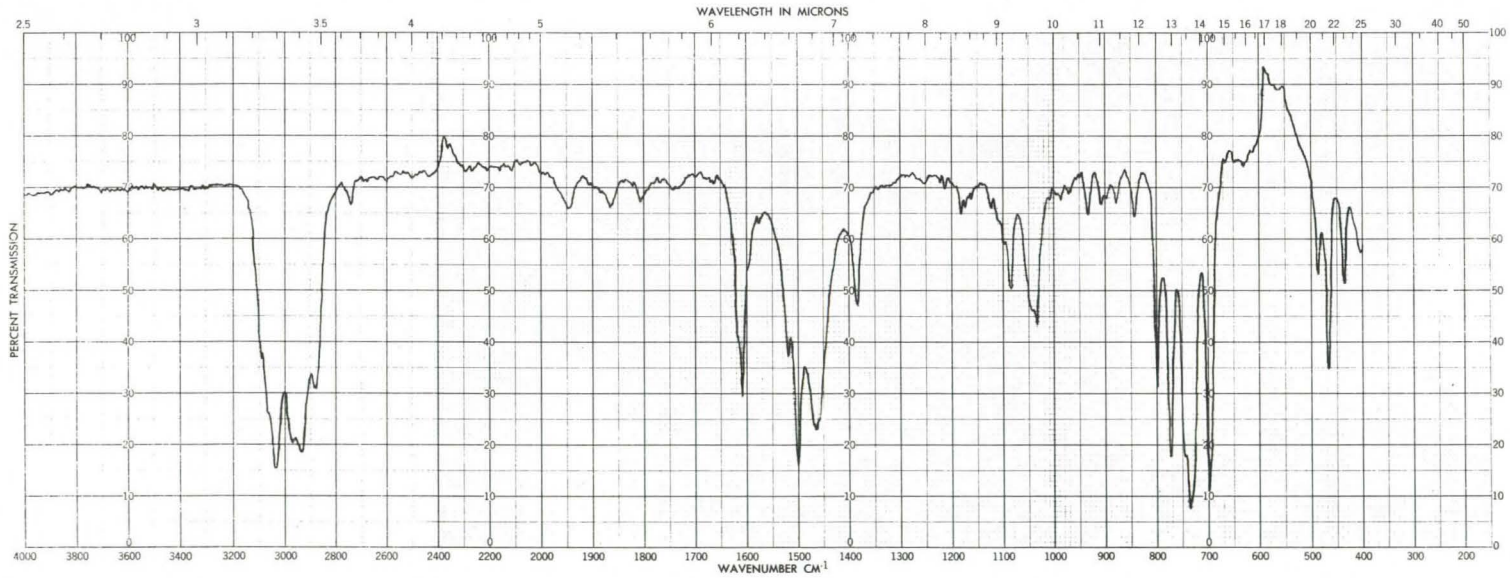
PAINT TYPE - M

(VEHICLE)

COLOR - WHITE
LAB NO 70-12897

GENERIC COMPOSITION:

OIL MODIFIED PHTHALIC ALKYD, MED.-LONG OIL



PAINT TYPE - M

(SOLVENTS)

COLOR - WHITE
LAB NO 70-12897

GENERIC COMPOSITION:

TOLUENE & XYLENES

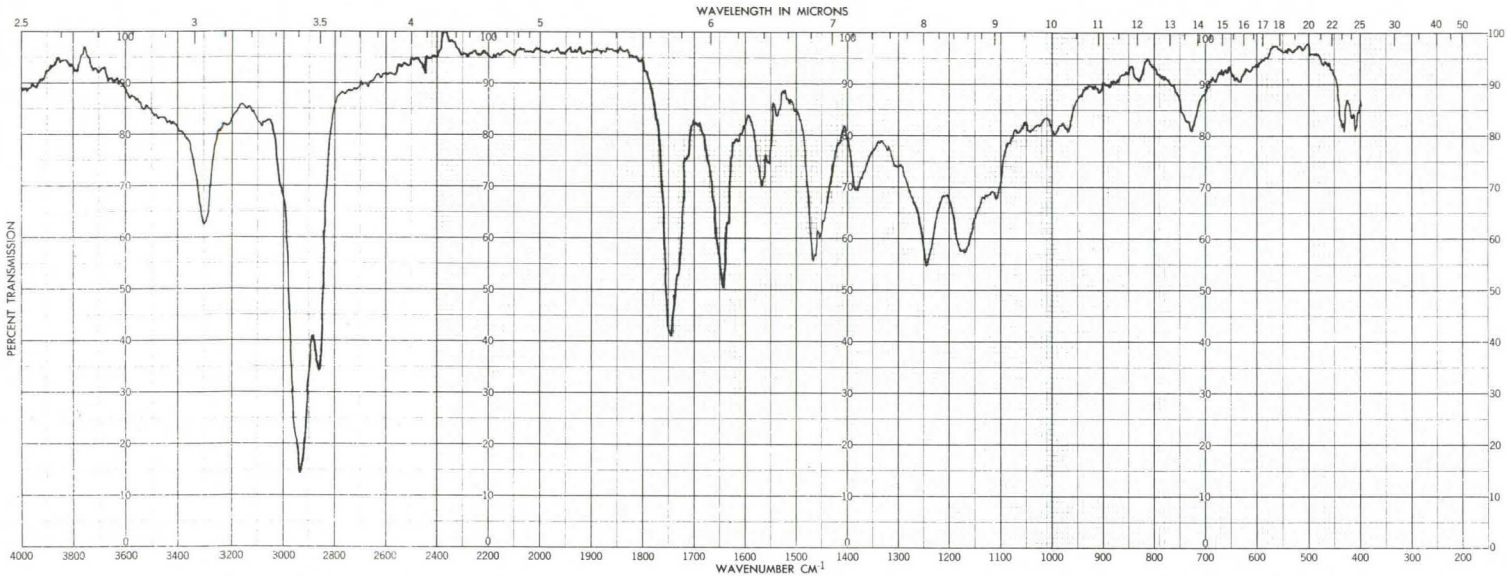


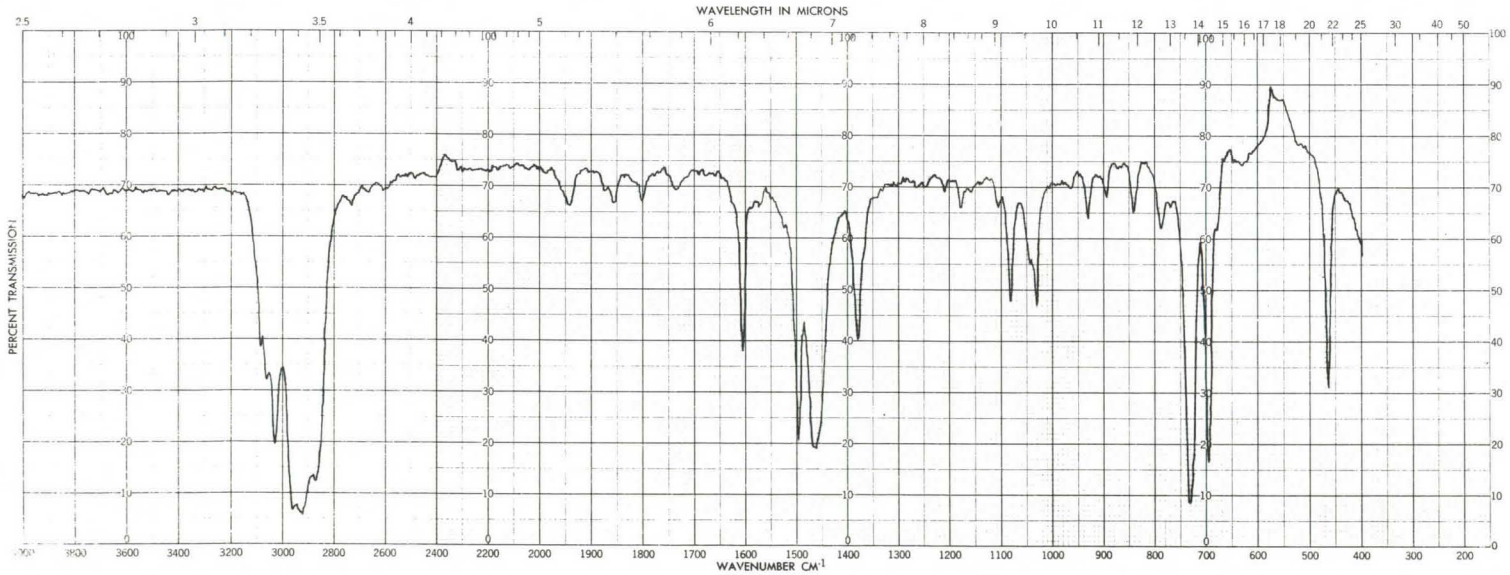
FIGURE 11

PAINT TYPE - O

(VEHICLE)

COLOR - YELLOW
LAB NO 70-12898

GENERIC COMPOSITION
OIL MODIFIED POLYAMIDE



PAINT TYPE - O

(SOLVENTS)

COLOR - YELLOW
LAB NO 70-12898

GENERIC COMPOSITION
TOLUENE

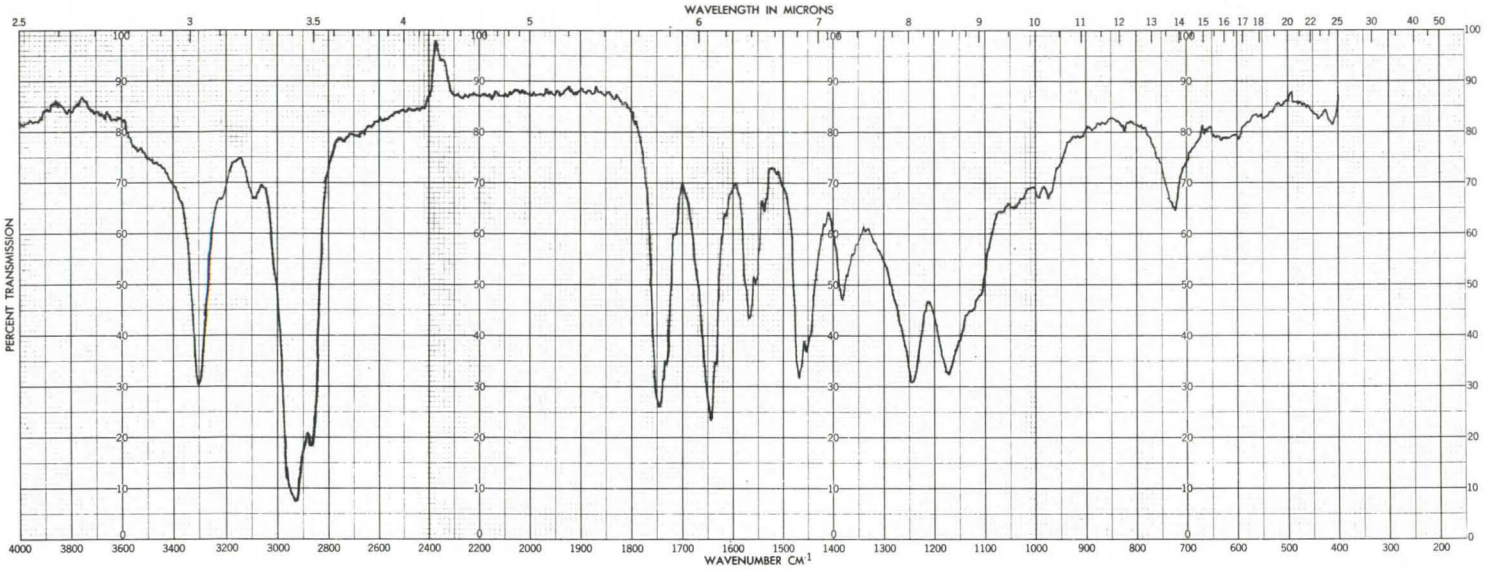


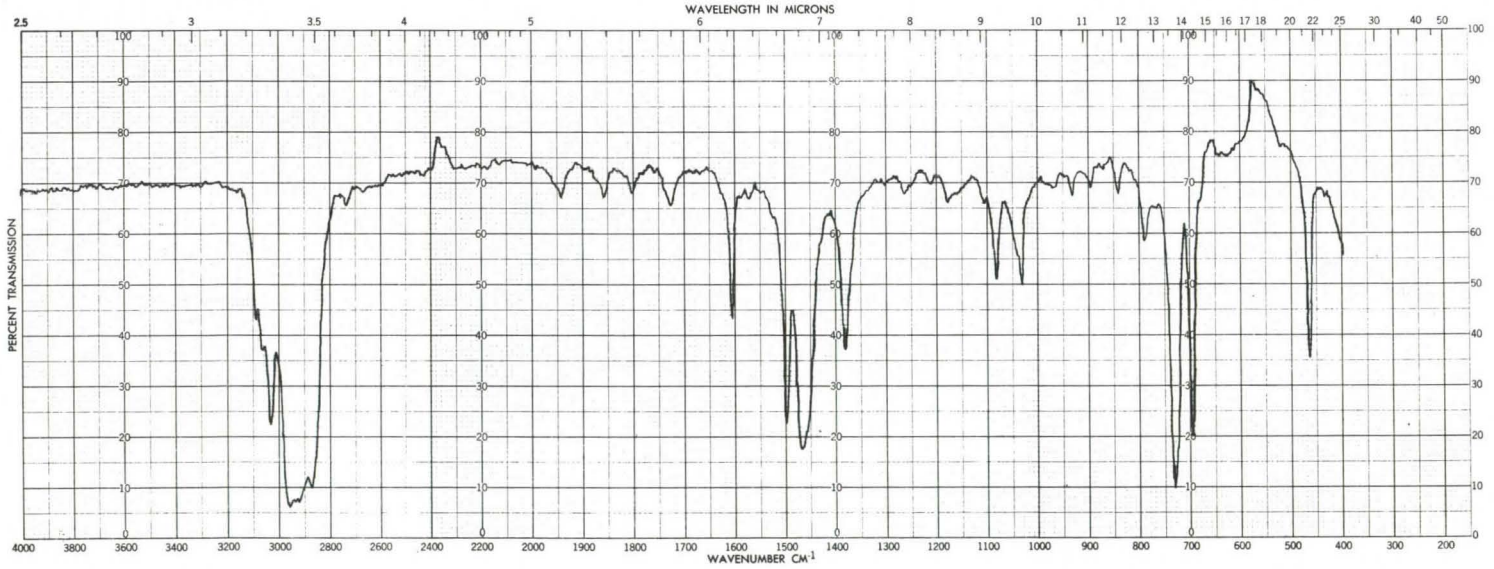
FIGURE 12

PAINT TYPE - O

(VEHICLE)

COLOR - WHITE
LAB NO 70-12899

GENERIC COMPOSITION:
OIL MODIFIED POLYAMIDE



PAINT TYPE - O

(SOLVENTS)

COLOR - WHITE
LAB NO 70-12899

GENERIC COMPOSITION:
TOLUENE