

Infrared Spectrum of Chlorofluoromethane

By Earle K. Plyler and Mary A. Lamb

In order to compare its spectrum with that of other halogenated methanes, the infrared spectrum of chlorofluoromethane has been measured in the gaseous state from 2 to 30 microns. The longest wavelength band was observed at 26 microns. Twenty-five bands have been observed with cells of 5, 60, and 100 centimeters in length and with gas pressures up to 80 centimeters of mercury. Nine of the observed bands have been classified as fundamentals, and the remaining bands are attributed to harmonics and combinations. Several bands in the region from 1.5 to 2.5 microns were measured on a high resolution grating instrument, and it was possible to resolve each of seven bands into a series of lines in this region. These bands are located at 1.657, 1.682, 1.700, 1.755, 2.229, 2.287, and 2.436 microns; the separation of the rotational lines is of the order of 2.3 cm^{-1} for these bands.

The infrared spectra of a number of substituted methanes have been measured by many observers.¹ The change in the spectrum when the halogens are substituted for the hydrogen atoms is marked, and there is a general shift of all the corresponding fundamental bands to longer wavelengths. When all the hydrogens of methane are substituted by the halogens, no fundamental bands occur at wavelengths less than 7μ . In the case of chlorofluoromethane the vibrations of the two hydrogens give rise to strong bands in the region of 3.5μ , and the contributions of the halogen to the vibrations occur in the region from 7 to 26μ . Of the nine fundamental bands, the one with longest wavelength is observed at 26μ . Seventeen harmonic and overtone bands are present in the spectrum when moderate amounts of the gas are measured. Thirteen of these bands were observed in the short wavelength region. The spectrum of chlorofluoromethane is similar to that of dichloromethane and difluoromethane. The locations of the nine fundamentals of these three compounds are compared, and it is found that the bands of chlorofluoromethane have characteristics similar to those of the corresponding bands of dichloromethane and difluoromethane.

The spectrum of chlorofluoromethane was measured from 2 to 30μ on a Perkin-Elmer infrared spectrometer using prisms of sodium chloride, lithium fluoride, potassium bromide, and thallium bromide-iodide. In the region of 1.5 to 2.6μ the spectrum was observed by the use of a grating spectrometer. A 15,000 line per inch grating with the ruling surface $7/4$ in. in width and $4\frac{1}{2}$ in. in height was used in the spectrometer, and a 1-m off-axis mirror was used for collimating the radiation. A PbS cell was used for the detector. The high resolution available with this instrument permitted observation of fine structure in some of the bands. The angular position of the grating was noted by a Veeder counter, and the readings were related to wavelengths by use of the higher orders of the emission lines of mercury. A Cetron mercury lamp, similar to the S-1 sun lamp, was used as the source. The image of one of the hot electrodes was focussed on the entrance slit, and the absorption spectrum was measured. Superimposed on the recorder trace of the chlorofluoro-

methane absorption spectrum were the mercury emission lines. With these observations the wavelengths of the absorption bands could be located accurately. The wavelength determinations for separate trials checked to about one part in 24,000. For higher resolution a tungsten ribbon lamp with a quartz window was used as the source. When it was operated at $2,700^\circ \text{K}$, it was possible to use slits of 0.025 mm in the $1.6\text{-}\mu$ region.

Three cells with thicknesses of 5, 60, and 100 cm were used for containing the gas. The different pressures of gas are recorded on the figures. The 100-cm cell, which was used in observing the $26\text{-}\mu$ band, had polyethylene windows, and could not be evacuated. It was filled by flushing with the gas, and the precise amount in the cell was not determined.

The chlorofluoromethane was supplied by Kinetic Chemicals, Inc. That it was of sufficient purity for absorption measurements was indicated by tests on the mass spectrometer. It was found to consist of 97.3 percent of chlorofluoromethane; the 2.7 percent is made up of related methanes. Comparison also was made with the infrared spectra of other substituted methanes, and none of the strong bands of these compounds were present in the spectrum of chlorofluoromethane with the cell thicknesses used in this investigation.

In figure 1 is shown the spectrum of chlorofluoromethane from 2 to 31μ . The region from 15 to 22μ , measured with a potassium bromide prism, has not been included in the figure since no bands were observed in this region when a 5-cm cell with a gas pressure of 50 cm of mercury was used. Two inserts of the bands at 4.72 and 7.40μ are included on an enlarged scale. The zero branches can be seen for both of these bands. The two CH_2 vibrations in the region of 3.5μ are sufficiently separated so that there is not a serious overlapping. Two small bands were observed in the region of 2.3μ with the 5-cm cell. When a 60-cm cell was employed, eight bands were found in this region and are shown in figure 2. The two bands at 2.4719 and 2.4840μ are not shown in the figure. They are of very low intensities, and only the zero branches appeared. At high resolution the rotational structure of the band at 2.2291μ is shown in the lower part of figure 2. In figure 3 the absorption bands in the region of 1.6μ , as observed

¹ G. Herzberg, Infrared and Raman spectra of polyatomic molecules (D. Van Nostrand Co., Inc., New York, N. Y., 1945).

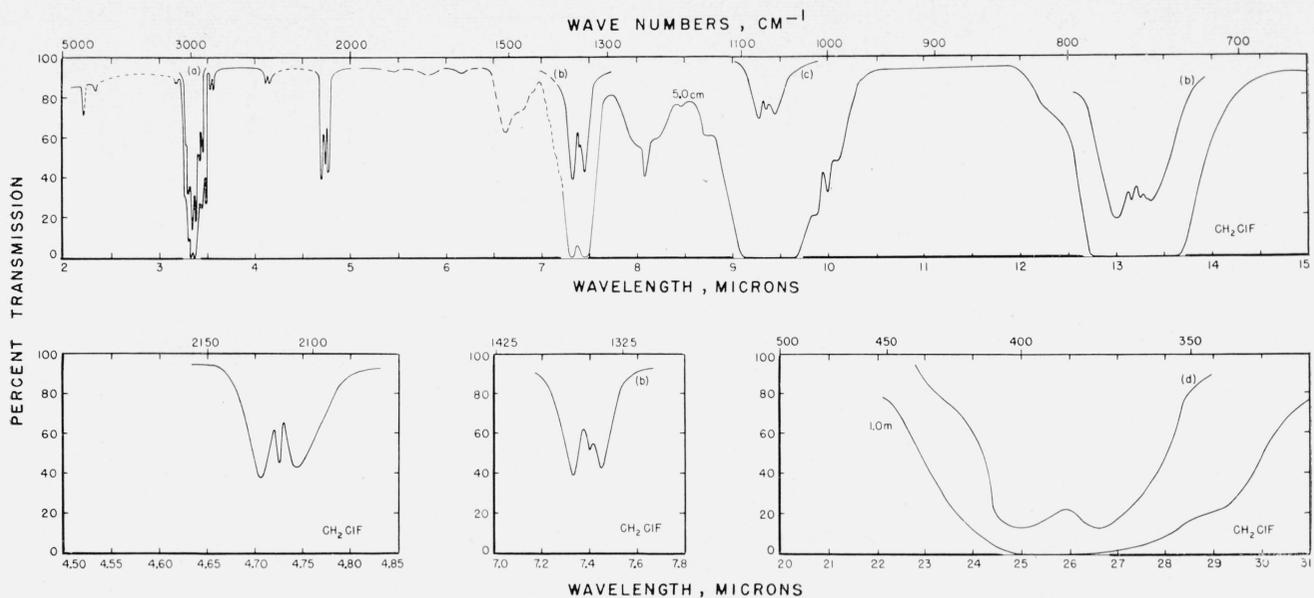


FIGURE 1. Absorption spectrum of chlorofluoromethane from 2 to 31 μ .

A 5-cm cell with a gas pressure of 50 cm of mercury was used from 2 to 15 μ . The gas pressure for insert (a) was 20 cm. (b) 4 cm, and (c) 0.5 cm of mercury, all in a 5-cm cell. From 22 to 31 μ , a 1-m cell with polyethylene windows was used. Since the gas pressure could not be measured in this cell, gas was flushed through it and thus the gas was at atmospheric pressure. For insert (d) some gas was removed from the 1-m cell. The bands at 4.72 and 7.40 μ are repeated on an enlarged scale.

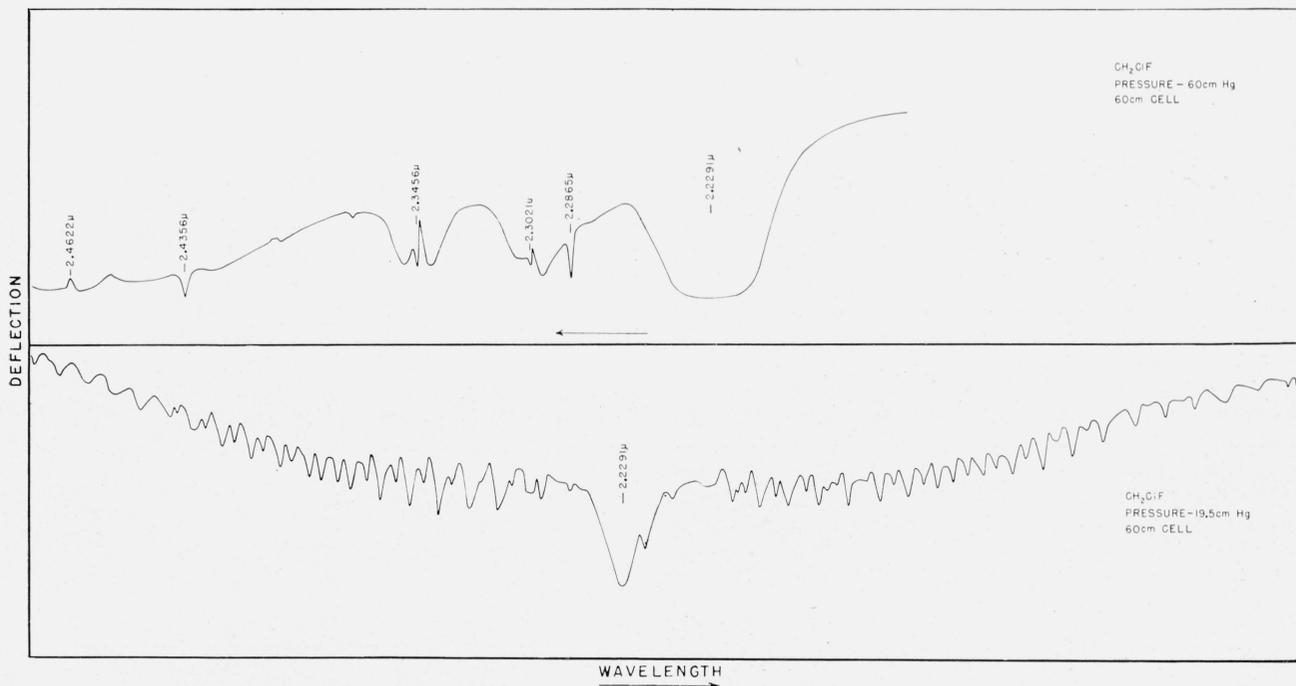


FIGURE 2. Absorption spectrum of chlorofluoromethane from 2.15 to 2.48 μ .

The lower curve is the band at 2.229 μ , as observed under high resolution.

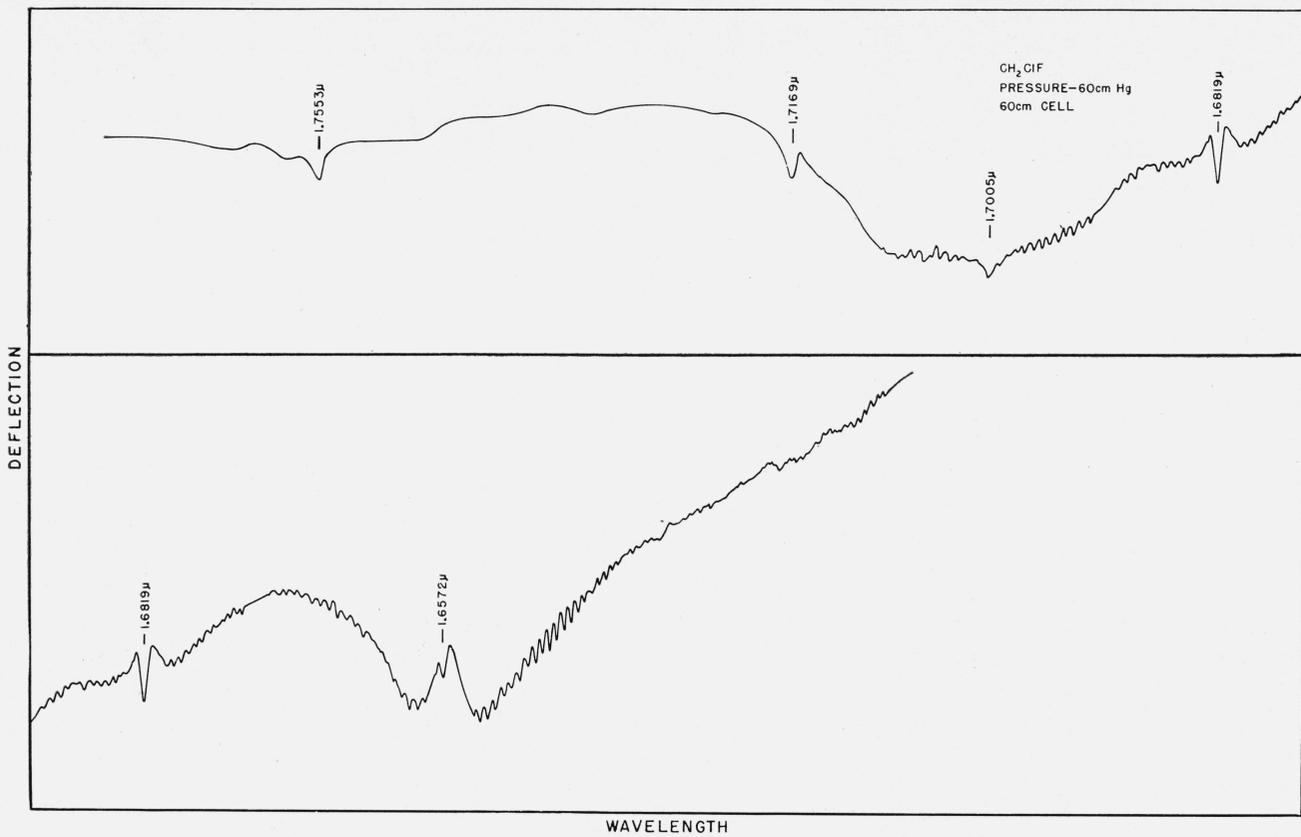


FIGURE 3. Absorption spectrum of chlorofluoromethane in the region of 1.60 to 1.78 μ .

The wavelengths of the centers of the six bands in this region are indicated on the figure.

with rapid scanning of the grating instrument, are shown. The low intensity band at 1.7880 μ is not shown in the figure. All the bands in this region include the 3.4- and 3.5- μ bands as combinations or harmonics. In figure 4 are shown the bands at 1.6572 and 1.7005 μ under high resolution. The emission lines at 1.6921, 1.7074, and 1.7110 μ on the lower part of figure 4 are from the mercury spectrum. The region between 2.5 and 3.0 μ should contain several combination bands. This region was not measured on the grating instrument, because of intense absorption due to atmospheric water vapor.

The nine fundamentals have been selected from the observed bands by making a comparison with the spectra of dichloromethane and difluoromethane. Except for the two bands in the region of 3.5 μ , all the fundamentals of chlorofluoromethane should have longer wavelengths than those for difluoromethane and smaller wavelengths than those for dichloromethane. The Raman spectrum also has been compared with the infrared spectrum, and it is found that the infrared band at 1,236 cm^{-1} was not observed in the Raman spectrum. The Raman value of 1,468 cm^{-1} is somewhat smaller than the wave number of the infrared band at 1,475 cm^{-1} , but because of the water vapor absorption in this region it was not possible to make an accurate determination of the

center of the band. The nine fundamental vibrations of chlorofluoromethane may be classified as two stretching vibrations of CH_2 (ν_1 symmetrical and ν_6 antisymmetrical) and the deformation of CH_2 , ν_2 . The C-Cl will have corresponding motions, which are ν_9 , ν_3 , and ν_4 bending or deformation. In addition there are three other vibrations, the torsional, ν_5 , and two rocking vibrations, ν_7 and ν_8 .

There is a close parallel between the infrared spectra of dichloromethane, difluoromethane, and chlorofluoromethane. In table 1 the fundamental frequencies of the three molecules are listed for the nine

TABLE 1. A comparison of the fundamental bands of dichloromethane, chlorofluoromethane, and difluoromethane

Assign- ment	Wave number (cm^{-1})		
	CH_2Cl_2	CH_2ClF	CH_2F_2
ν_4	283	385	529
ν_3	704	760	1,090
ν_9	737	1,000	1,120
ν_7	899	1,068	1,176
ν_5	1,155	1,236	1,262
ν_8	1,266	1,351	1,435
ν_2	1,429	^a 1,468	^a 1,508
ν_1	2,984	2,993	2,949
ν_6	3,048	3,048	3,012

^a Raman value.

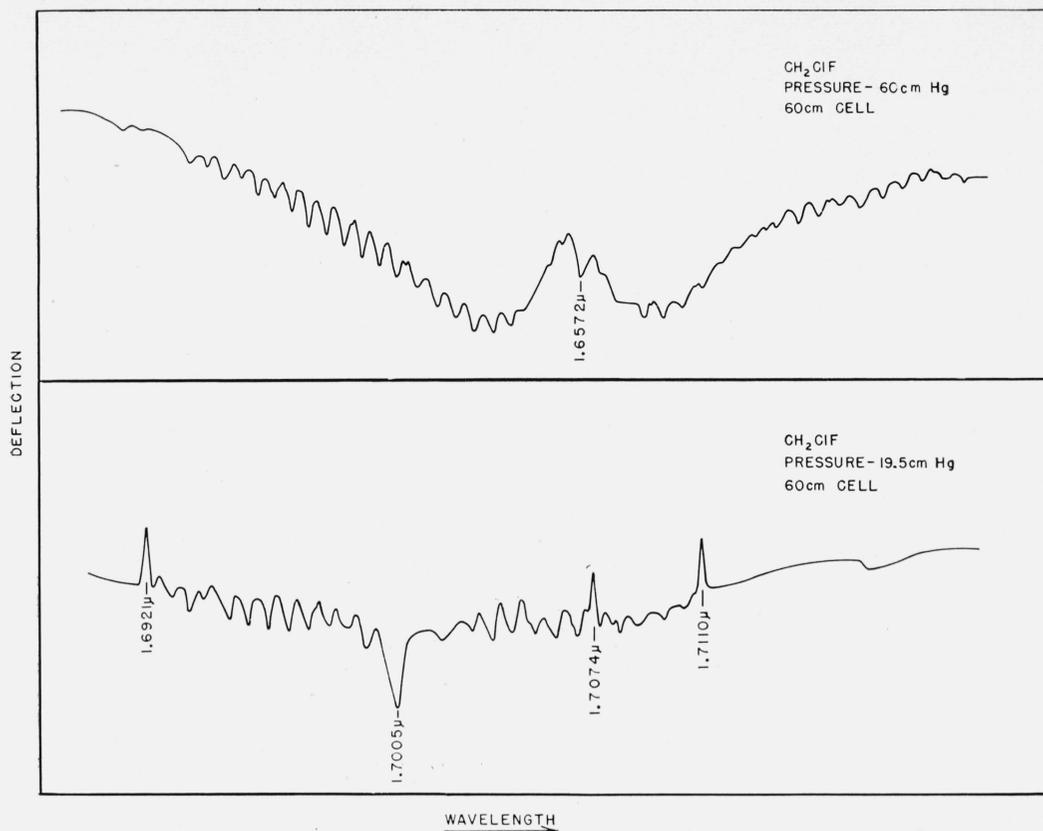


FIGURE 4. Absorption spectrum of chlorofluoromethane in the region of 1.6572 and 1.7005 μ under high resolution. The emission lines on the lower curve, 1.6921, 1.7074, and 1.7110 μ , are produced by the mercury spectrum and are used for reference wavelengths.

types of vibrations involved. The classification of the bands of dichloromethane follows the assignments of Herzberg² from the data of C. Corin and G. B. B. M. Sutherland.³ The classification of chlorofluoromethane and difluoromethane have been made on the basis of assignments for dichloromethane.

The experimental values were obtained on the same instruments for the three molecules. H. B. Stewart and H. H. Nielsen⁴ have recently classified the bands of difluoromethane and assigned the torsional frequency as 1,511 cm^{-1} , instead of 1,262 cm^{-1} as in this work, and the band at 1,262 cm^{-1} observed in this work is missing in Stewart and Nielsen's data (see footnote 4). All bands involving the motions of the fluorine atom in chlorofluoromethane should be found at wave numbers between those of the corresponding bands in difluoromethane and dichloromethane. This is true for the assignments in table 1.

It is interesting to note that the CH_2 stretching vibrations of difluoromethane have wave numbers

that are less than in chlorofluoromethane. This indicates that the fluorine atoms may decrease the binding force in the CH_2 group. The CH_2 deformation vibration in difluoromethane is of very low intensity and was not observed, and the value 1,508 cm^{-1} is used from Raman data. This mode of vibration appears as a weak band at 1,475 cm^{-1} in chlorofluoromethane in the infrared spectrum.

In table 2 is given a list of the observed bands and their classifications. After the fundamentals were selected, the harmonic bands were classified. It was found that fairly large anharmonic terms caused the observed bands in the region of 1.6 μ to vary by 50 cm^{-1} or more from being twice the wave number of the fundamental. However, the band shapes were of assistance in the classification. For example, the small zero branch shows that the band at 1.7005 μ is the harmonic of the ν_1 band, which is the symmetric motion of the two hydrogens. The other intense band is classified as $2\nu_6$, and the combination band, $\nu_1 + \nu_6$, has a wave number between the values for the two harmonic bands. On the short wavelength side of the strong bands in the 3.4- μ region is a small band that arises from the second harmonic of ν_7 , $3\nu_7$. This

² See p. 317 of footnote 1.

³ C. Corin and G. B. B. M. Sutherland, Proc. Roy. Soc. (London) **165**, 43 (1938).

⁴ H. B. Stewart and H. H. Nielsen, Phys. Rev. **75**, 640 (1949).

TABLE 2. Classification of observed bands in chlorofluoromethane

Assignment	Intensity	Wave-length	Wave number (vacuum)
		μ	cm^{-1}
ν_4	M	26.0	385
ν_3	VS	13.16	760
ν_9	M	9.99	1,001
ν_7	VS	9.36	1,068
ν_8	M	8.09	1,236
ν_5	S	7.40	1,351
ν_2	W	6.78	1,475
$\nu_3 + \nu_7$	M	4.725	2,115
$\nu_2 + \nu_7 + 2\nu_9$	VW	4.141	2,414
$\nu_2 + \nu_8$	VW	3.544	2,821
$2\nu_2$	M	3.434	^a 2,911
ν_1	MS	3.340	^a 2,993
ν_6	M	3.280	^a 3,048
$3\nu_7$	VW	3.184	3,140
$\nu_1 + \nu_7$	VVW	2.4841	4,025
$\nu_6 + \nu_7$	VW	2.4719	4,044
$\nu_1 + \nu_3 + \nu_4$	VVW	2.4622	4,060
$\nu_6 + \nu_3 + \nu_4$	W	2.4356	4,105
$\nu_6 + \nu_5$	W	2.3456	4,262
$\nu_4 + \nu_6$	VW	2.3021	4,343
$\nu_1 + \nu_6$	M	2.2865	4,372
$\nu_2 + \nu_6$	MS	2.2291	4,485
$\nu_1 + \nu_6 + \nu_2$	VVW	1.7880	5,591
$2\nu_8 + \nu_6$	VW	1.7553	5,695
$2\nu_2 + \nu_1$	VW	1.7169	5,823
$2\nu_1$	M	1.7005	5,879
$\nu_1 + \nu_6$	W	1.6818	5,944
$2\nu_6$	MS	1.6572	6,032

^a Raman value.

is the only second harmonic band observed in the spectrum when the 5.0-cm cell was used and indicates that ν_7 is very intense. The first harmonic band of ν_2 is fairly intense in the infrared spectrum, and this increase in intensity is brought out by resonance with ν_1 at 2,993 cm^{-1} . In the spectrum of dichloromethane $2\nu_2$ is weak, as the conditions of resonance are not so favorable.

The resolution of some of the bands in the regions of 1.6 and 2.4 μ into their rotational structures makes it possible to determine one of the moments of inertia for the molecule. The separation of the rotational lines varies slightly from one band to another. The average spacing of the lines is about 2.4 cm^{-1} in the 1.7005 μ band. A study of the rotational structure of this molecule and that of dichloromethane and difluoromethane is being made and will be the subject of another report.

The spectrum of chlorofluoromethane supports the assignments of the fundamental bands made on the spectrum of dichloromethane. Further experimental work will be necessary to have sufficient data for determining the CCIF angle in this molecule.

WASHINGTON, April 14, 1950.

Resin Bonding of Hardwood Fibers in Offset Papers

By Bourdon W. Scribner, Merle B. Shaw, Martin J. O'Leary, and Joshua K. Missimer

A further investigation was made of the application of resin bonding to the development of strength in offset papers made principally of short hardwood fibers that develop little strength by the conventional beating. Melamine-formaldehyde resin was used. The papers were made from hardwood pulps produced at the U. S. Forest Products Laboratory in experimental study of the pulping of aspen, black gum, paper birch, and beech. The pulps were prepared by the mechanical, sulfate, soda, sulfite, and neutral sulfite processes. By the use of the melamine resin, papers having good strength and resistance to pick, combined with low expansion and curl, were produced with very little beating. The pulps that gave the best results comprised aspen sulfate, aspen soda, aspen sulfite, birch sulfite, and black gum sulfate. Resin-bonded papers containing 75 percent of these pulps compared favorably with papers made in the conventional way with the usual 50 percent of commercial hardwood fibers. An appreciable increase in the proportion of hardwood fibers used in offset papers would greatly extend pulpwood resources.

I. Introduction

Effective utilization of large quantities of hardwoods is an outstanding pulpwood problem. The pulp and paper industry has had an amazing growth during this century, but the supply of the more generally used pulp woods is steadily decreasing. Wood is the most important source of paper-making material. Pulp produced from coniferous or needle-leaved trees (softwoods), such as spruce, fir, and pine, is used to a much greater extent than that produced from the hardwood or broad-leaved trees, such as the various "poplars", birch, beech, gum, etc., commonly used for pulping. The use of hardwoods for pulping is good forestry practice, and in regions having a large volume of hardwood species or inferior trees unsuited for lumber or similar products is an economic necessity.

In comparison with spruce and other softwoods, however, the use of hardwoods has been limited by the characteristics of the hardwood fibers. The characteristics that affect the manufacture of paper vary in kind and quantity with different woods. One differentiation is the length of fiber, which is approximately from 1 to 1.5 mm for hardwoods and from 2.5 to 4.5 mm for coniferous wood. The fiber of the hardwood trees also has a structure that is different from that of the conifers. Its soft and absorbent texture renders it useful for bulky papers such as certain classes of printing paper, but it is not as strong as the softwood fiber.

The strength of paper depends on the strength of its fibers and on the adhesive bond between them. Cellulose is a colloid. It gelatinizes ("hydrates") on beating it in water and thus causes gel-like bonds to be formed between the fibers of the finished sheet.