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THE AGING CHARACTERISTICS
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PEAN HANDMADE PAPERS (1400-1800)

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THE AGING CHARACTERISTICS OF EUROPEAN HANDMADE PAPERS (1400-1800)

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ABSTRACT

European handmade papers in both good and poor condition made in the period of 1400-1800 have been examined using both nondestructive and limited destructive testing methods. The elastic properties of the well-preserved papers were considerably higher than those papers in poor condition. It was suspected that these papers might be gelatin sized. Elastic property measurements on gelatin sized filter papers demonstrated that gelatin could be responsible for the high values of elastic constants found for papers in good condition. Using Chromato Scanner and Fourier Infrared Transform Infrared Spectroscopy techniques, it was estimated that the papers in good condition had a gelatin content of about 10-12%; the poor papers also contained gelatin, but at a lower level, i.e., 3-5%, and possibly in a degraded state. Measurements of pH revealed that the good papers were alkaline, while the poor papers were acidic. The latter situation is attributed to possible inferior papermaking techniques, i.e., increasing alum usage may also play a role. Fiber strength is also estimated to be lower in the poor papers.

KEYWORDS: Aging, pH, Gelatin, Ultrasonic, Sizing, Mechanical Properties, Zero Span, Fiber Length, FTIR, Chromato Scan.

INTRODUCTION

This paper is concerned with the aging behavior of 15th-18th century European handmade papers. The report focuses on the role that nondestructive testing played in an extensive investigation initiated and conducted by Barrett (1). The main thrust of the study by Barrett was to determine if there was anything special about the pulping and stock treatment characteristics which contributed to the longevity typical of these types of papers. Waterhouse's involvement, in addition to advising on the nondestructive testing of the above papers, was to try to determine if nondestructive testing could be used to discriminate between naturally aged papers in good and poor condition.

This paper is mainly concerned with explaining the differences in physical properties of good and poor papers based on nondestructive testing. The possibility of monitoring the extent of aging nondestructively has been the subject of a recent paper by Waterhouse (2).

An understanding of the excellent natural aging characteristics of some of these early papers might be helpful in improving the archival survival of modern day papers. This is a problem; in fact, since the advent of modern papermaking, many early documents and books are now in an advanced state of decay. The Library of Congress has six million volumes which are in that condition (3). The major factor which has lead to this demise is the acidic state of the paper resulting from rosin acid sizing. Therefore, there has been considerable effort in recent years to develop alkaline papermaking as a viable alternative. Accelerated aging test results are certainly encouraging, but unfortunately, only time will tell if this is a satisfactory solution!

Storage conditions can have a significant effect on the life expectancy of paper. In principle, if a pollution free, low temperature and low humidity environment can be maintained, and if the paper is not subjected to cyclic changes in temperature and humidity, its life expectancy would be greatly improved. In this case the storage and environmental conditions are not known with any certainty, and therefore, the differences we report might simply be attributed to environmental differences the papers have experienced, rather than being due to differences in raw materials, pulping, or stock treatment.

Flax is the main fiber component of early European handmade papers. Possible fiber preparation and treatment for these papers is detailed elsewhere (1). In addition, as confirmed in this study gelatin is also present. Its primary role is as a sizing agent, although it can also have a significant impact on the paper's mechanical properties (4).

EXPERIMENTAL

Samples of European handmade papers over the period of 1400-1800 in good and poor condition were obtained by Barrett (1). Good papers were characterized by having a high aesthetic quality, good color and formation, freedom from knots and specks, the absence of foxing, and a good state of preservation. The poor papers suffered from one or more of the above defects and were in a poor state of preservation.

The in-plane and out-of-plane specific engineering moduli were determined using equipment developed at the Institute of Paper Science and Technology (formerly The Institute of Paper Chemistry) (5-6). Apparent density calculations were based on soft caliper measurements (7).

Fourier Transform Infrared Spectroscopy (FTIR) measurements were made at IPST using a Nicolet Instrument. The quantitative assessment of gelatin content was determined using a diffuse reflectance procedure developed by Berben, Rademacher, Sell, and Easty, (8).

The presence of gelatin, the effects of aging, and furnish type were also investigated by Barrett (1) using a Shimadzu Dual-Wavelength Thin-layer Chromato Scanner Model CS-930, manufactured by Shimadzu Corporation, Tokyo, Japan.

Procedures for Kajaani fiber length, zero span, metals analysis, and pH measurements are detailed elsewhere (1).

RESULTS AND DISCUSSION

A summary of the nondestructive tests made on the samples in good and poor condition is given in Table 1. There are several interesting points to note. The differences between the samples in good condition and poor condition are very significant despite the large variability in the measurements. Typical coefficients of variation for in-plane and out-of-plane elastic constants of today's machine-made papers are in the range of 3-5% (see Table 3). We also note that the samples in poor condition show more variability than those in good condition. The directionality or grain, as measured by the ratio of elastic properties, is also significant in both sets of handmade papers.

The out-of-plane moduli for the good papers are particularly high by comparison with today's printing and writing papers. The question is whether one could attribute the differences found, between the good and poor papers, directly to aging. One might expect to see some change in elastic properties as a result of aging, but perhaps not to the extent shown in Table 1.

Table 1. Summary of Ultrasonic Measurements on Historical Papers.

#	Date	Grammage	Density	E/rho (km/sec)^2	C.V.	Ez/rho (km/sec)^2	C.V.	R
Samples in good condition:								
17	1400	85.4	0.638	6.16	10.1	0.389	10.1	1.56
12	1483	91.8	0.869	6.07	14.7	0.419	8.2	1.13
		96.4	0.742	5.83	10.2	0.455	6.6	1.41
1	1685	78.7	0.819	6.07	9.2	0.275	14.2	1.23
2	1701	74.6	0.823	6.13	8.5	0.334	8.8	1.39
3	1704	84.6	0.793	6.43	10.7	0.317	4.1	1.27
Samples in poor condition:								
39	1590	61.5	0.797	3.16	16.9	0.042	26.0	1.36
32	1685	89.1	0.907	2.86	13.4	0.064	17.5	1.34
35	1695	62.5	0.769	2.84	13.8	0.068	12.4	1.47
46	1710	75.8	0.720	3.60	15.2	0.137	9.5	1.21
44	1711	70.6	0.847	2.99	11.1	0.058	11.6	1.32
		71.6	0.840	3.20	11.8	0.062	16.3	1.65

At this stage we knew that other furnish components such as gelatin were present but did not know their level or possible effect on the physical performance of the sheet.

We therefore decided to make some measurements on handmade paper which had been prepared by Barrett (1). Handsheets were made both with and without gelatin addition. The results are shown in Table 2. Densification appears to have only a small effect on the control sheets; however, there is a significant increase in the out-of-plane modulus. Gelatin addition is more effective than wet pressing in increasing the out-of-plane modulus and is most effective at the low density level. It is also interesting to note that the modulus values of the poor papers are similar to those for sheets without gelatin addition, whereas the modulus values of the good papers are similar to those for sheets with gelatin addition. The mean in-plane modulus values of Barrett's papers lie between the values for the good and poor papers.

Table 2. Summary of Ultrasonic Measurements on Barrett's Handmade Papers.

#	Grammage	Density	E	C.V.	Ez	C.V.	R
B6	75.5	0.528	2.53		0.067	13.3	
B6G	131.4	0.518	4.41		0.254		
B4	87.3	0.628	3.03		0.152	13.2	
B4G	90.0	0.658	4.30		0.360		

The high levels of out-of-plane modulus for the papers in good condition suggest that the gelatin is present at a significant level. In unpublished research on the effect of additives on out-of-plane modulus, Waterhouse (9) has found that at low levels of polymer addition, e.g., starch and p.a.e., the increase in out-of-plane modulus is small.

We therefore needed to determine the level of gelatin in the handmade papers shown in Table 1. Perhaps the differences in physical properties and condition could be ascribed to the presence or absence of gelatin. The two techniques used to determine the level of gelatin present were the Chromato Scanner (ultraviolet spectroscopy) and FTIR (Fourier Transform Infrared Reflectance Spectroscopy) described in the experimental section. The former technique was used to give a qualitative indication of the amount of gelatin present and how the spectrum was affected by both natural and accelerated aging, while the latter was used to determine quantitatively the amount of gelatin present.

A typical Chromato Scan taken and redrawn from reference (1) is shown in Figure 1. The curve designated L4 is flax only, while L11 is gelatin and alum sized. L11 aged shows the effect of accelerated aging. We note in Figure 1 an increase in the area under the curve due to gelatin addition, and that aging appears to reduce this area. Furthermore, an increase in the slope of the base line also occurs. An example of Chromato Scans taken on papers in good and poor condition is shown in Figure 2. Although the historical samples are in no way related, the poor sample shows a much lower area under the curve and increased slope similar to the control samples made by Barrett (1). The inference is that there is a significant amount of gelatin present in the good sample, and that the poor sample either did not initially contain the same level of gelatin as the good sample, or that degradation processes resulted in effectively lowering its content. In hindsight the Chromato Scan method appears to have the potential for quantitative analysis of gelatin content.

To calibrate the FTIR instrument, and to determine the effect of gelatin level on the out-of-plane modulus, a series of gelatin impregnated filter papers were prepared by Barrett. The properties of these papers are summarized in Table 3.

Table 3. Properties of Gelatin Sized Filter Papers.

Sample #	Total Grammage g/m^2	Total Density g/cm^3	Gelatin %	Ez (km/sec)^2	C.V. %
Control	74.1	0.441	0	0.099	5.3
2C	75.1	0.458	1.35	0.190	3.7
2P	76.5	0.478	3.24	0.201	3.0
3C	83.4	0.484	12.55	0.317	4.4
3P	87.4	0.518	17.95	0.319	6.9
4C	76.9	0.462	3.78	0.200	4.0
4P	81.8	0.473	10.39	0.223	4.5
5C	77.2	0.457	4.18	0.193	3.6
5P	77.7	0.463	4.86	0.203	3.9
6C	83.6	0.521	12.82	0.337	3.0
6P	82.3	0.537	11.07	0.322	5.3

C denotes a complete filter paper disc, and P denotes a partial filter paper disc, i.e., part of the disc had already been removed for other tests.

The variation of longitudinal out-of-plane modulus with gelatin content is shown in Figure 3. The correlation is quite good having an $r^2 = 0.81$. We also note that a gelatin level greater than 12% would be required to yield modulus values in the range of the good papers shown in Table 1, i.e., 0.277-0.455 (km/sec)^2. However, it should be emphasized that the filter paper furnish is not the same as the historical samples. Furthermore, the filter papers have a lower total density than the samples shown in Table 1 and the handsheets made by Barrett shown in Table 2. The high apparent density level of the sheets shown in Table 1 could possibly be attributed to either more extensive beating and/or possible "calendering" effects during finishing or printing.

The FTIR Spectroscopic results for the filter papers are given in Table 4.

Table 4. FTIR Results.

Sample	Gelatin %	IR Area	Corrected IR Area	Predicted Gelatin %
Control	0	18.4	0	-
2% GEL.SOLn	3.24	65.6	65.6	-
5% GEL.SOLn	12.55	94.0	75.6	-
Good Papers				
# Date				
1 1685		103.6	69.6	9.74
2 1701		118.6	84.6	12.10
12 1483		110.1	76.1	10.80
Poor Papers				
35 1695		58.6	24.4	2.71
39 1590		86.8	52.8	7.12
44 1711		80.1	46.1	6.07

As shown in Table 4 a relatively high level of gelatin is present in both the good and poor papers, although the level is significantly lower for the papers in poor condition. In addition to determining gelatin content, the FTIR spectrums indicate some evidence of gelatin degradation in the poor papers as shown in Figure 4, i.e., samples P44 and P35. We speculate that this degradation could be caused by acid hydrolysis.

We had initially thought that one of the reasons for the large difference in elastic properties between the papers in good and poor condition might be attributed to the presence or absence of gelatin. However, in addition to possible inferior papermaking strategies, i.e., the use of increasing amounts of alum over the centuries, it is also likely that adverse storage and environmental conditions might be responsible.

Measurements of pH by Barrett (1) which are summarized in Table 5 tend to support the above contention, i.e., the good papers are on the alkaline side, while the poor papers are acidic. Significant compositional differences which cannot be attributed to environmental changes are born out by the extensive metals analysis conducted by Barrett (1) employing PIXE (Proton induced x-ray emission) and XRF (X-ray Fluorescence) techniques. In summary, he found that higher levels of magnesium, calcium, and zinc are present in the good papers, while sulphur, chlorine, potassium, aluminium, copper, and iron are greater in the poor papers. It is hypothesized that airborne sulphur could be added as a post manufacturing component.

Table 5. Surface pH Measurements.

	Century	Mean pH	No. of Specimens
Good			
	15th	7.2	8
	16th	6.4	8
	17th	6.5	13
	18th	5.5	40
Poor			
	16th	5.5	4
	17th	5.4	20
	18th	4.7	36

Barrett (1) also made measurements of fiber length and strength, using the Kajaani fiber length analyzer and IPST zero span jaws, respectively. These are summarized in Tables 6-7.

Table 6. Kajaani Fiber Length Measurements.

Century	weighted 1	Weighted 2	Arithmetic	No. of Samples
Good Papers				
15th,	1.11	1.91	0.52	8
16th,	0.98	1.81	0.42	7
17th,	0.89	1.61	0.37	14
18th,	0.83	1.40	0.41	40
Poor Papers				
16th,	1.23	2.11	0.59	4
17th,	1.12	2.01	0.48	21
18th,	0.92	1.60	0.45	40

Table 7. Zero Span Strength Measurements.

Sample Date	Grammage g/m^2	Mean Zero Span Nm/g	Weighted Fiber Length mm
Good Papers			
1400	79.6	83	1.76
1685	79.2	111	0.81
1701	73.9	108	0.81
1704	86.9	107	0.86
Poor Papers			
1590	62.0	88.0	1.07
1685	87.7	74.0	0.85
1695	65.6	66.0	1.20
1710	73.2	77.0	1.00
1711	71.1	81.0	1.16
Barrett Handmade Papers			
174 B4	87.3	-	-
172 B4G	90.0	122.0	-
175 B6	75.5	-	-
173 B6G	131.4	103.0	-

Fibers taken from the papers in poor condition tend to be longer than those taken from the papers in good condition. This difference in length is attributed to selection of more tender rags and or more extensive retting and beating of the furnish used to make the good papers. On the other hand, the zero span results generally show, but not unequivocally, that the papers in poor condition have a lower zero span strength than those in good condition. Page (10) has shown with accelerated heat aging that zero span strength falls as aging progresses. It is also interesting to note in Table 7 that limited zero span measurements made on the Barrett handsheets are in fairly close agreement with the values obtained for the papers in good condition.

CONCLUSIONS

European handmade papers in both good and poor condition made in the period of 1400-1800 have been examined using both nondestructive and limited destructive testing methods. The main objective of the study was to determine the factors responsible for the differences found in their condition. Good papers were characterized by having a high aesthetic quality, good color and formation, freedom from knots and specks, the absence of foxing, and a good state of preservation.

Using nondestructive measurements large differences in the elastic properties of papers in both good and poor condition were found. In particular, the out-of-plane elastic modulus of the papers in good condition was considerably higher than those typical of modern day printing and writing papers.

Using both Chromato Scan and FTIR spectroscopic technique, it was also found that the papers contained gelatin, which is estimated to be in the range of 10-12% for the good papers and 3-5% for the poor papers. Also the Chromato Scan and FTIR spectra indicate that the gelatin present in the poor papers is in a degraded state. It is not known whether the papers in poor condition initially contained a higher percentage of gelatin or whether the poor condition is due to differences in formulation and/or environmental and storage conditions. Nevertheless, it was concluded that the high levels of gelatin (and in a better state of preservation) are responsible for the high values of elastic modulus.

Metal analysis by PIXE and XRF together with pH measurements suggest that raw material, e.g., alum and handsheet making practices, are in part responsible for the condition of the poor papers. Storage and environmental conditions play a key role in controlling paper properties, i.e, aging, but unfortunately, in this case they are unknown for both sets of papers.

Fiber strength appears to be significantly lower in the poor papers. However, interpretation of the zero span measurements is complicated by the fact that the fiber length in the good papers is lower than in the poor papers. It is presumed that fiber strength has been lowered by acid hydrolysis.

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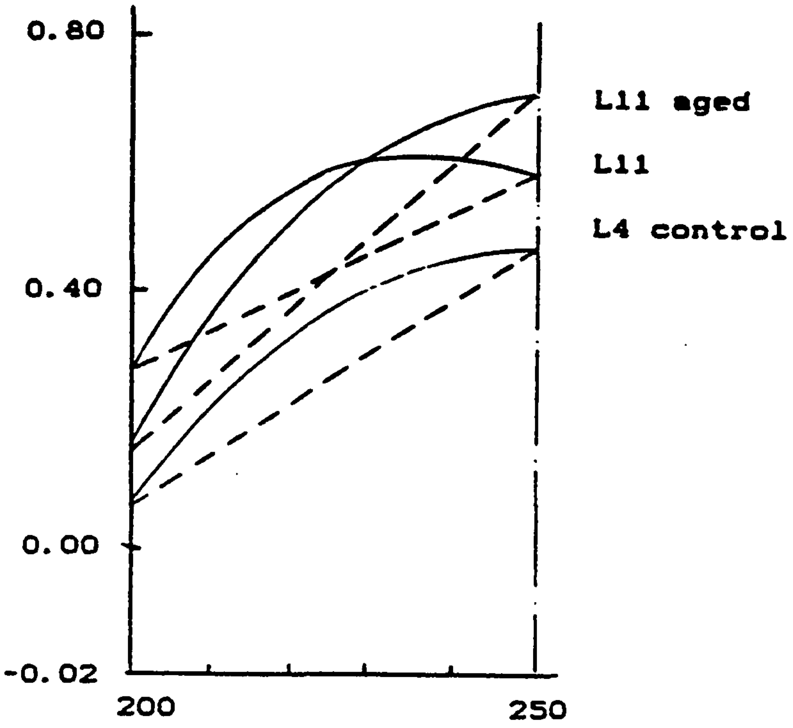
LIST OF FIGURES

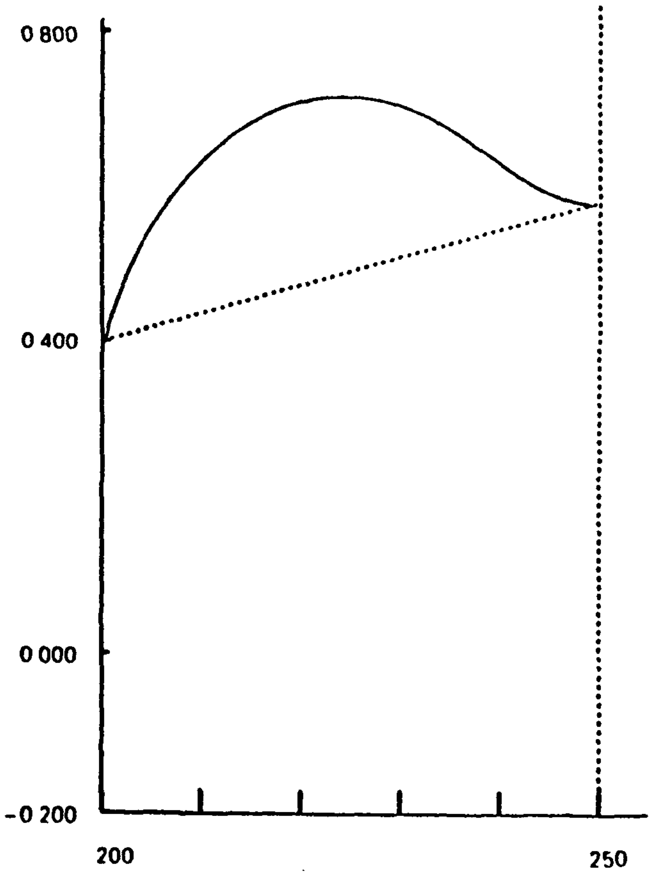
Figure 1. Chromato Scanner Plot showing absorption in the 200-250nm UV wavelength range. Vertical axis represents "optical density" in plotter units. L4 fermented flax control, L11 fermented flax gelatin and alum sized, L11 aged.

Figure 2. Chromato Scanner Plots showing absorption in the 200-250nm UV wavelength range of European handmade papers in good G17 and poor P35 condition.

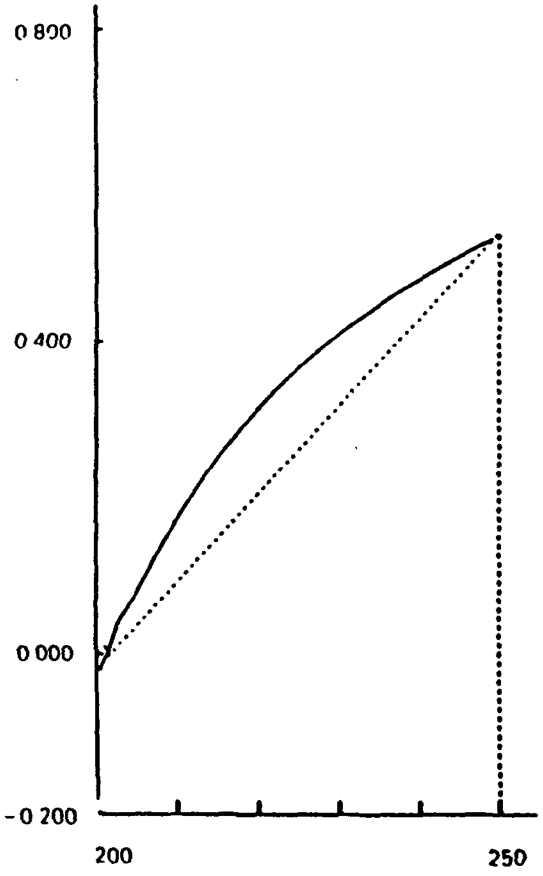
Figure 3. Variation of out-of-plane modulus with % gelatin content for gelatin impregnated filter papers.

Figure 4. Fourier Transform Infrared Spectrums of Gelatin, Flax papers with and without gelatin addition, and European handmade paper in good and poor condition.


0.80
0.40
0.00
-0.02
200
250
L11 aged
L11
L4 control

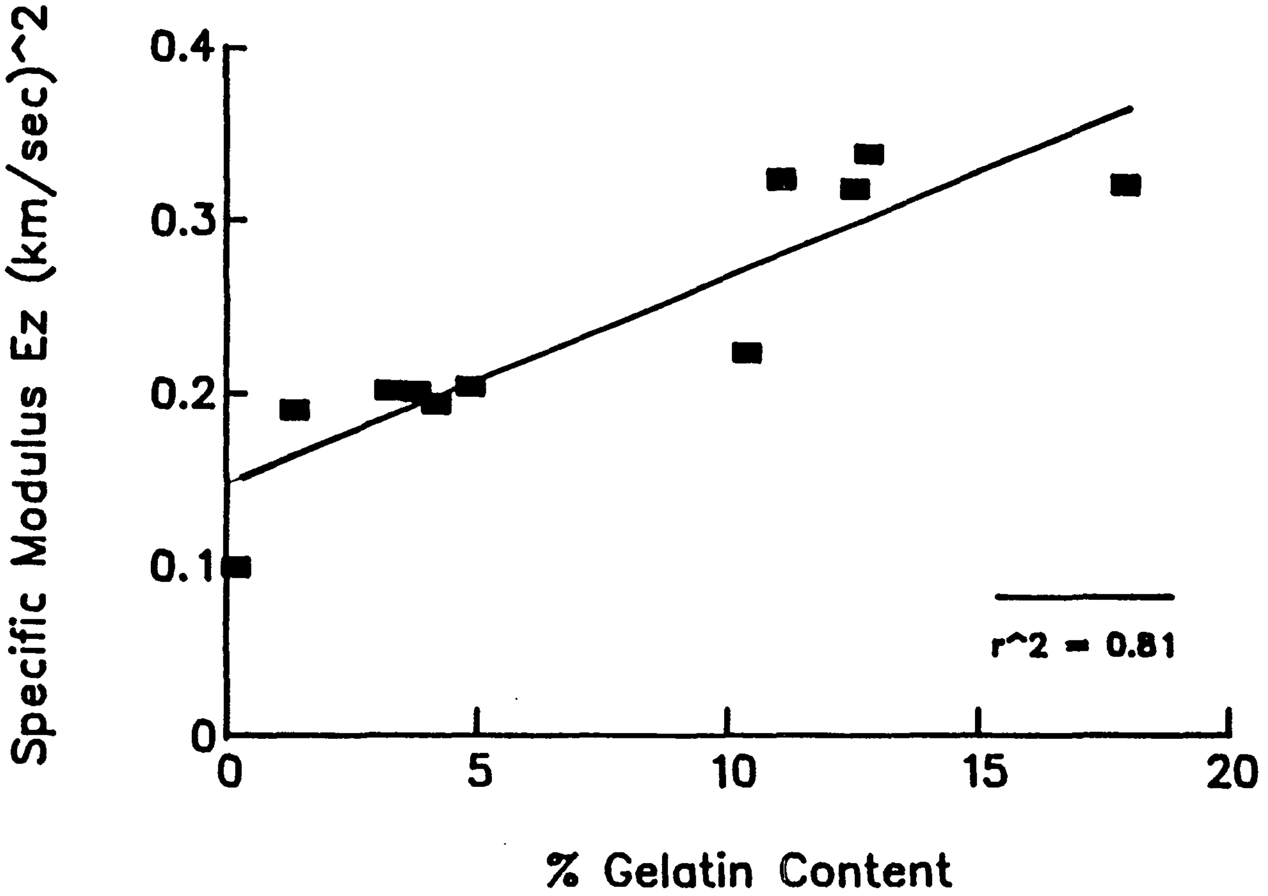


Good G17

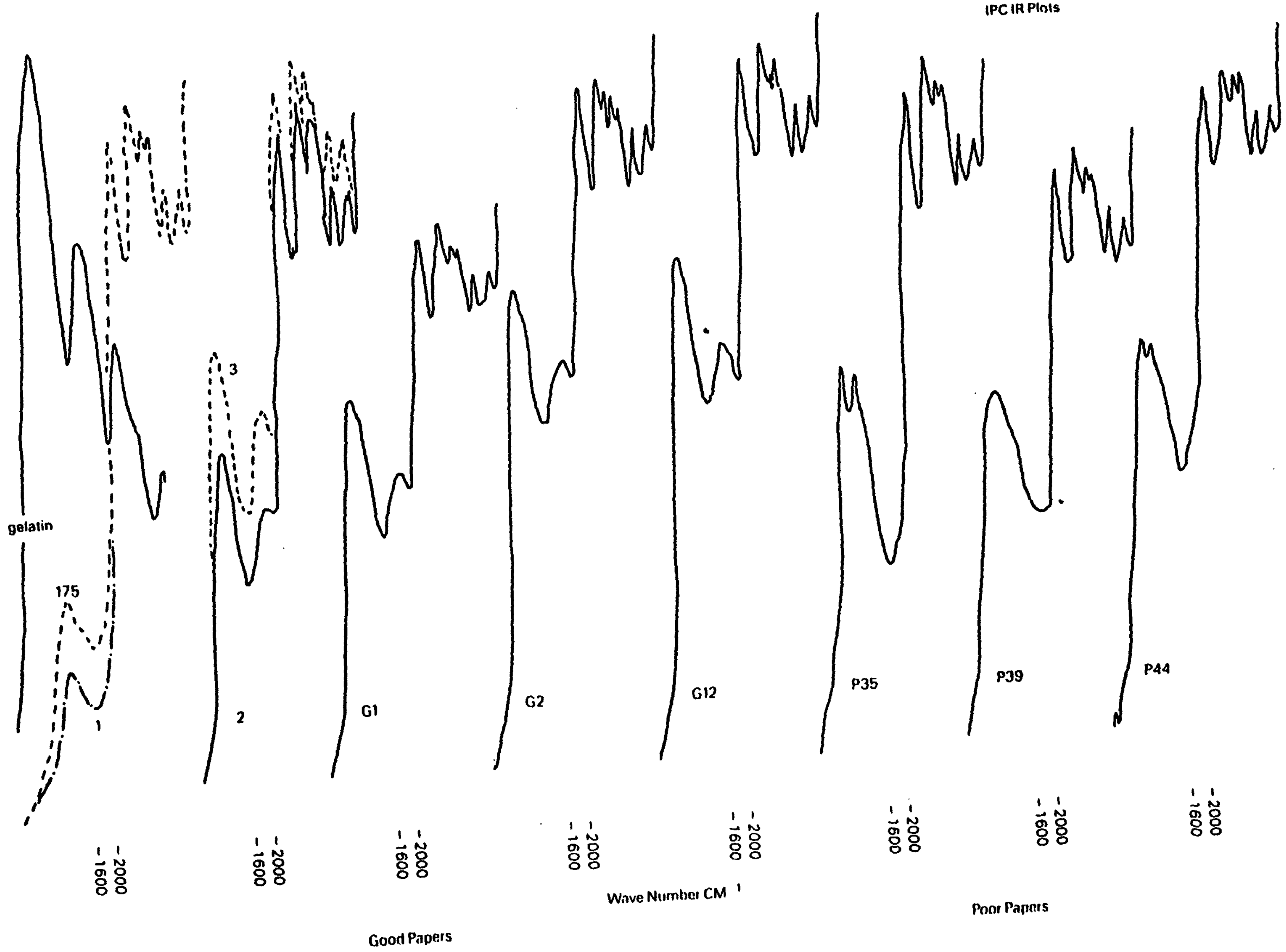


Poor P35

VARIATION OF OUT–OF–PLANE MODULUS WITH GELATIN CONTENT – FILTER PAPERS



IPC IR Plots


gelatin
175
1
3
2
G1
G2
G12
P35
P39
P44
- 2000
- 1600
Wave Number CM ⁻¹
Good Papers
Poor Papers