The Effect of Varying Degrees of Carboxylation on Picking Resistance - A Study of Carboxylated Latexes

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THE EFFECT OF VARYING DEGREES OF CARBOXYLATION ON PICKING RESISTANCE - A STUDY OF CARBOXYLATED LATEXES

BY

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ABSTRACT

A carboxylated latex is formed by substituting carboxylic acid groups onto styrene/butadiene latex particles, thus displacing the emulsifying agent to a certain degree. This will lead to a more stable system with increased binding power for use in coating systems. The purpose of this study was to determine how variations in the degree of carboxylation affect the IGT picking resistance of a coated sheet.

The experiment consisted of making nine different coating formulations with both latex addition level and degree of carboxylation being varied. These formulations were applied to a paper substrate by the use of the Keagan coater. Testing of the sheets was done on the IGT Pick Resistance tester.

Results of testing indicate that as the degree of carboxylation increases, the resistance to picking increases as well. Data also indicates that after the initial carboxylation occurs, the rate at which the picking resistance increases levels out to a certain extent.

KEYWORDS:
IGT Pick, Latex, Carboxylation, Coating

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INTRODUCTION:

For years, the primary adhesives used in the paper industry to bind pigment particles to the paper substrate were starch and protein. Although starch and protein were and still are excellent adhesives, there are limitations. Industry focused attention on developing a new adhesive system, and in 1937, latexes were introduced to the paper industry.

While latexes have been used for almost fifty years, variations to the basic latex particle have occurred, and one such variation is termed a carboxylated latex. These forms of latex have only been around about fifteen to twenty years, and are relatively new. It is for this reason that this paper deals with carboxylated latexes, and how variations in the degree of carboxylation affects the picking resistance of a coating.

In order to make the best possible product for a customer, it is essential to understand what results may be achieved. The printing industry and the paper industry go hand- in- hand. The IGT pick resistance test simulates the action of a printing press and gives a relative sample of how well a coating will withstand the picking action which occurs in the printing press. By studying the relationship between the degree of carboxylation and the resistance to pick it is possible to obtain better results by simply changing the amount of carboxylation in a coating formulation.

The purpose of this study is to determine what the relation- between the degree of carboxylation and pick resistance is.

THEORETICAL DISCUSSION:

What is a latex? Vanderhoff and Bradford have defined a latex to be the product of an emulsion polymerization involving vinyl monomers dispersed in an aqueous, water phase. A latex is the spherical particles of the polymer suspended as a colloid in the water phase (1). Latexes can be divided into three major groups: styrene/butadienes, polyvinyl acetates, and acrylics. Styrene/butadiene latexes will be the only latex reviewed.

Styrene/butadiene latexes are composed of both styrene and butadiene groups. Haig and Heiser have shown in their research that the styrene will lend hardness and dimensional stability to the particle. Butadiene will contribute elasticity, flexibility, tackiness, and softness to the polymer particle (2). By varying the ratio of styrene to butadiene, different properties may be achieved.

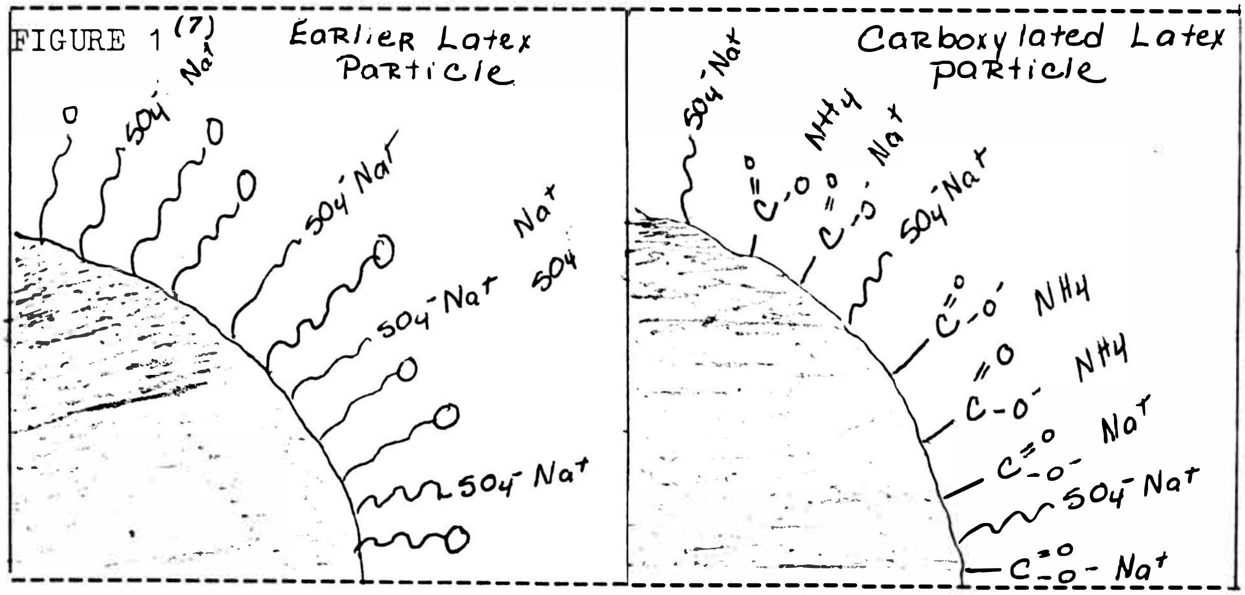
By addition of unsaturated carboxylics or other monomers, it is possible to modify the styrene/butadiene polymer particle. The resulting product is termed a carboxylated latex. Research in the field of carboxylated latexes has shown that these latexes have greatly improved properties over those of non-carboxylated latexes.

Currently, Dow Chemical USA, a leader in the manufacture of latexes, markets over eight types of carboxylated latexes due to the increased demand in the paper industry (3,4,5,6). Different styrene/butadiene ratios and type of carboxylic acid or monomer added produce many variations of carboxylated latexes.

There are many reasons for the increased use of carboxylated latexes in coating formulations. Carboxylated latexes have decreased dependency upon pH, require no post-stabilization, have increased binding power, increased blade performance, increased glueability, improved wet rub, and excellent starch compatibility (7). Carboxylation also improves the resistance to picking (3). Before discussing the above mentioned properties, it is important to understand the method of carboxylation.

Figure 1 illustrates a non-carboxylated latex and a carboxylated latex. The non-carboxylated latex is almost completely sulfonated. The addition of carboxylic acid groups displace the sulfate groups thus allowing for a more stable structure to form. Two explanations have been proposed to account for this. First, when the carboxylic groups attach to the polymer surface, some extend into the aqueous phase and then ionize. This allows for a "shell" of water to form around the particle. The hydrophilic, ionized carboxylic groups act the same as a non-ionic surfactant does to a non-carboxylated latex

FIGURE 1 (7)



system. Second, the ionized groups are charged, and are repulsed from other similar groups. This repulsion leads to a more rigid structure (7). Thus, it can be clearly seen why carboxylated latexes do not require post-stabilization by a surfactant. Since a surfactant is not required, the soap content of the system will be lower and will not adversely affect the wet rub resistance.

The binding power of the carboxylated latex is improved as a result of the greater polarity of the latex particle, as well as the adhesive particles wetting the pigment surfaces more readily than non-carboxylated latexes (7).

Greater water holding capabilities help to improve the blade coater performance of the carboxylated latex. Non-carboxylated latexes tend to de-water too quickly and result in scratching, streaking, and other common blade coater problems. Carboxylated latexes also have the advantage of being able to run at higher solids level. Non-carboxylated latexes are restricted to low solids levels due to rheological problems. Dilatancy is a problem frequently encountered (3).

Glueability refers to the ability of the adhesive to "glue" or bind the coating system together. Glueability problems are not encountered when using starch or protein as a binder. Problems arise when using synthetic polymer particles. A comparison of carboxylated latexes to non-carboxylated latexes, reveals that the carboxylated latexes have improved glueability but still have problems (2).

The stability of the carboxylated latex particles serves to minimize the dependency upon pH adjustment. Carboxylated

latexes can efficiently operate in a wide pH range.

The resistance of paper to picking can be defined as a function of the surface layer which withstands the force of separation of the sheet from the inked surface. This force acts perpendicularly to the surface plane forcing the coating to break away or rupture from the surface plane. It has been indicated that carboxylation will increase the resistance to picking. Exactly how it is increased is the topic of this thesis study.

To briefly summarize, carboxylated latexes are formed from styrene/butadiene particles and carboxylic acid groups or other monomers. The negatively charged carboxylic acid groups displace the negatively charged sulfate ions on the particle surface. As a result, a more uniform colloidal dispersion will occur. The product, a carboxylated latex, has decreased dependency upon pH, does not require post-stabilization by a surfactant, has increased binding power, blade performance, glueability,and wet rub. Compatibility with starch and improved picking resistance is also achieved. The purpose of this study is to determine what the relationship between the degree of carboxylation and the picking resistance is.

EXPERIMENTAL PROCEDURE:

OUTLINE OF EQUIPMENT/ CHEMICALS/ MATERIALS USED

I. Equipment:

A. Coating of Sheets

1. Mixers
2. Mixing Containers
3. Brookfield Viscometer
4. pH Meter
5. Thermometer
6. Keagan Coater

B. Testing of Coated Sheets

1. Paper Cutter
2. IGT Pick Resistance Tester

II. Materials/Chemicals:

A. Latexes

1. Carboxylated latex with 4% carboxylation
2. Carboxylated latex with 10% carboxylation
3. Compatible latex with 0% carboxylation

B. Clay - Hydrafine, a #2 fine clay

C. Calcium Carbonate - Hydrocarb 30, a precipitated calcium carbonate

D. Paper Stock - 43.5 lb/rm sheet

COATING FORMULATIONS

I. Clay - mixed at 65% solids

II. Calcium Carbonate - mixed at 65% solids

III. All coating formulations adjusted to 55% final solids

IV. Latexes:

A. 6-0 = 6pph latex addition level, 0% carboxylation

B. 6-4 = 6pph latex addition level, 4% carboxylation

C. 6-10 = 6pph latex addition level, 10% carboxylation

D. 9-0 = 9pph latex addition level, 0% carboxylation

E. 9-4 = 9pph latex addition level, 4% carboxylation

F. 9-10 = 9pph latex addition level, 10% carboxylation

G. 12-0 = 12pph latex addition level, 0% carboxylation

H. 12-4 = 12pph latex addition level, 4% carboxylation

I. 12-10 = 12pph latex addition level, 10% carboxylation

V. Other Latex Specifications:

	1	2	3
Acrylic Acid	0%	4%	10%
Styrene	56%	58%	52%
Butadiene	44%	38%	38%
Particle Size	2500Å	1250Å	1150Å
% Solids	48%	50%	46%

LABORATORY PROCEDURE:

Nine different coatings were formulated and mixed up. Each formulation consisted of clay, calcium carbonate, and an appropriate latex. The initial base coating, before the latex was introduced, was composed of 80% clay and 20% calcium carbonate. More detailed descriptions of the clay, calcium carbonate, and latexes may be found on the two preceding pages. Both the clay and the calcium were mixed up separately at 65% solids based on the dry weight of the pigment. The latexes were premixed and the % solids is shown on the preceding page.

Latex addition to the base coating was based on 200g dry pigment with the solids content of the latex being taken into account. After the addition of the latexes at either 6,9, or 12pph addition level, the final coatings were adjusted to 55% solids by the addition of water. The coatings were then thoroughly mixed with standard laboratory mixers.

After mixing, the temperature, pH, and Brookfield viscosity (at 20 and 100 rpm) of the coatings were recorded. A #2 spindle was used in the viscosity test for all formulations. This data may be found in Appendix 1.

The Keagan coater was used to apply the coating mixtures to the paper substrate. The coating was placed into the coating pan and metered off by an attached blade.

The coated sheets were allowed to dry, condition, and then trimmed to obtain more uniform surfaces. The sheets were supercalendered at a pressure of 33 psi with two passes through the nip.

The sheets were cut into 1½ inch strips with machine direction running in the long direction of the strips. It was essential that all strips be cut in this manner to obtain meaningful results.

Before the strips were cut, however, the basis weight of the uncoated stock and the coated stock needed to be obtained in order to determine coat weight.

IGT Pick tests were run on the IGT Pick Resistance tester, model number IGT AC2 using IGT viscosity oils. Testing was carried out by following the manufacturer's suggested procedure. A TAPPI Standard for this test does not exist, only a recommended method which involves an older model.

Specifications for the tests are as follows:

Latex Addition Level	6pph	9pph	12pph
Speed	1.0 m/s	2.0 m/s	3.0 m/s
Force	35 Kgf	45 Kgf	55 Kgf
Oil - Viscosity	low	low	medium

The results of the tests were recorded using a chart to determine where picking began.

RESULTS AND STANDARD VALUES:

Data obtained from the IGT Pick Resistance tests can be found in Appendix 2. Data has also been graphed for easier analysis. Data from the coater run is available in Appendix 1.

Inspection of the graphs in Appendix 2 are somewhat deceptive. In order to understand what is occurring, it should be noted that many points were duplicated in testing. Each level of carboxylation on each graph incorporates 60 data points

thus it is important to review the appropriate data sheets when viewing the graphs.

Other data was not represented graphically due to a lack of significance to the central theme.

Refer to Appendices for test results.

DISCUSSION OF RESULTS:

Analysis of the data in Appendix 2 clearly shows that there is a direct relationship between the degree of carboxylation and the picking resistance of a coating. Thus, when the degree of carboxylation increases, so does the resistance to picking. As picking resistance is a function of the binding power and glueability of a coating system; and the binding power and glueability increase with carboxylation, it is possible to theorize that carboxylation will increase the picking resistance. The data also indicates that after the initial carboxylation occurs, the rate of increase in the resistance to pick compared to the degree of carboxylation slows down. Thus, rather than a "straight" line relationship, it is more of a curve with the rate of change increasing rapidly at first then slowing down to a slow, but gradual change. At the different levels of latex addition, the above mentioned relationship exists.

Analysis of the data also indicates that the picking resistance is a function of latex addition level. Thus, the coating with 12pph latex addition is stronger than the coating with only 6pph latex. This can be easily explained. The more

adhesive present in the system will result in more binding of particles to other particles as well as increased binding of particles to the paper substrate. This trend was expected to occur due to the nature of adhesives.

One relationship that can not be easily explained or eliminated from this study is the influence of particle size on the picking resitance. Refering to page 7, part V, it can be seen that there is a dramatic difference in particle size as the carboxylation changes. One problem initially encountered when working with carboxylated latexes is that other properties are changed when the degree of carboxylation is changed. This is the case with particle size, which will give the same results if plotted graphically against the picking resistance. The smaller the particle, the more particles will be present at the same weight. In this experiment there is no way to minimze the possible effect.

Variations in coat weight may also affect the final results. The greater the coat weight, the more particles present, thus increased binding will occur. The effect can be minimized by using equipment with less inherent variations.

CONCLUSIONS:

If the variations in particle size and coat weights are ignored, it can be stated that as the degree of carboxylation increases, the resistance to picking will also increase due to increased binding in the particle system as well as to the paper substrate. When carboxylation initially occurs, the

rate of change in picking resistance is greater than when additional carboxylation occurs. Thus , it can also be stated that the rate of change in the picking resistance is dependent upon the initial and final degree of carboxylation.

RECOMMENDATIONS:

Further work in this area would need to take in account the affect of particle size on the picking resistance. The affect of coat weight variations could be greatly reduced by using equipment for coating the paper which imparted a more uniform surface without fluctuations. The final recommendation involves obtaining a greater number of samples to understand the relationship better.

LITERATURE CITED

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APPENDIX 1

DATA FROM COATING RUN

Latex/ % Carboxylation	Temp. (^oF)	pH	Brookfield Viscosity * 20rpm	100rpm	Ave. Coat Wt. lbs/rm
6-0	62	7.55	1.25	9.25	8.10
6-4	63	7.30	1.25	9.80	8.13
6-10	62	6.75	1.50	11.25	8.11
9-0	63	7.20	1.50	12.70	8.74
9-4	64	7.30	1.10	9.60	8.08
9-10	62	6.60	2.00	12.90	8.13
12-0	64	7.15	1.50	12.50	8.41
12-4	64	7.30	1.17	14.30	8.67
12-10	64	6.70	2.00	14.00	8.29

* #2 spindle used for readings

APPENDIX 2

DATA
IGT PICK RESISTANCE
cm/sec

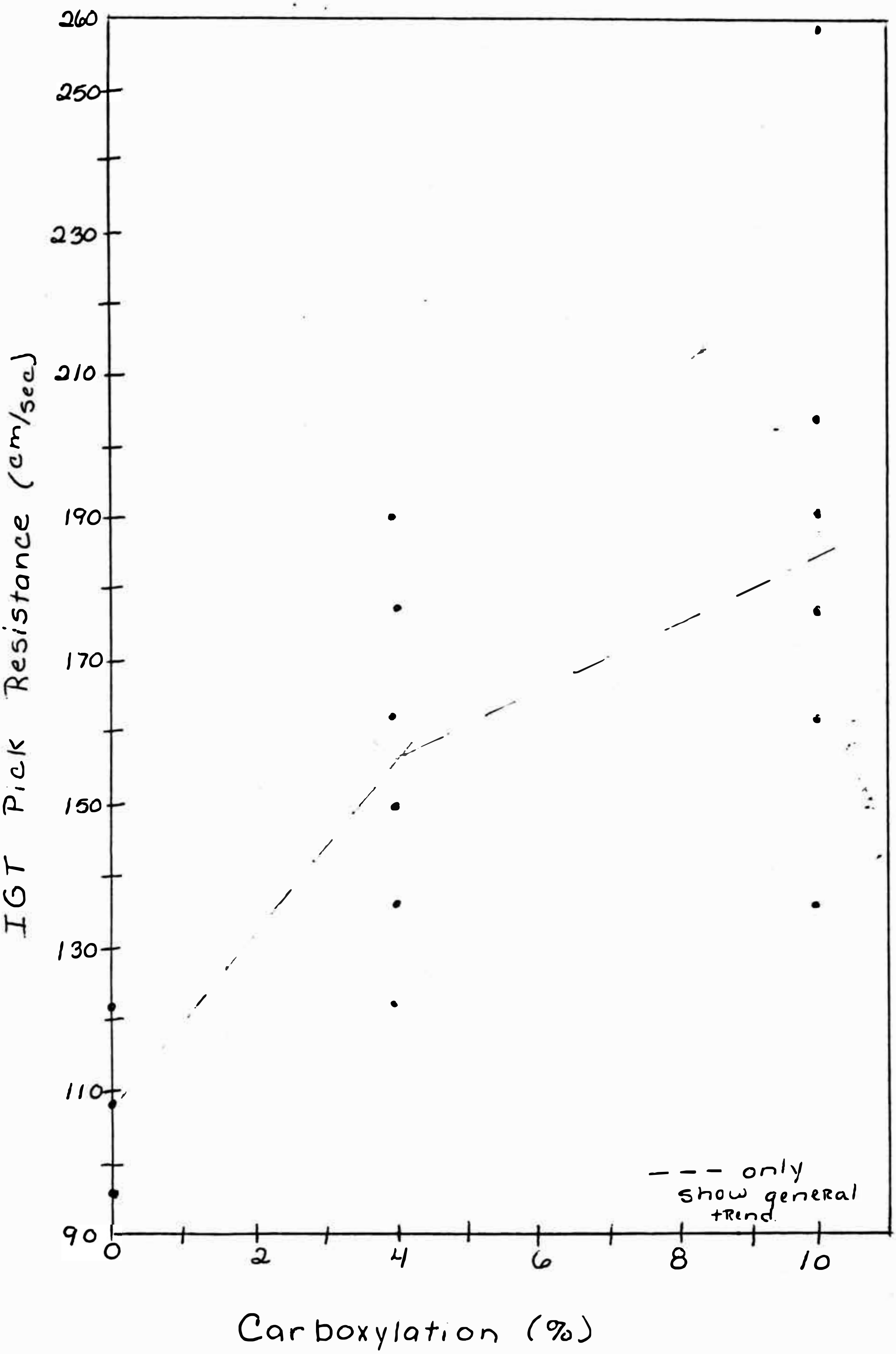
12-0	12-4	12-10
123	150	204
96	123	163
96	177	191
109	163	191
96	177	136
123	163	163
96	123	177
96	163	177
106	136	177
96	163	259
109	177	177
96	150	191
96	163	177
109	163	177
96	177	191
96	123	204
96	150	177
109	163	191
109	177	191
96	163	191
109	163	177
109	163	204
96	123	163
123	163	259
123	150	191
96	163	177
96	163	177
96	177	177
109	177	191
109	163	204
96	177	191
96	163	191
109	163	177

DATA
IGT PICK RESISTANCE
cm/sec

12-0	12-4	12-10
109	177	204
109	191	191
96	163	191
96	163	177
96	163	191
109	204	177
109	150	191
109	150	177
96	163	177
96	177	191
96	177	191
96	163	191
96	163	177
109	123	163
123	150	163
123	163	177
109	163	191
109	177	177
123	150	204
96	163	191
96	163	177
96	150	177
109	163	191
109	163	177
96	177	204
96	177	191
109	163	191

Speed = 3 m/sec
Force = 55 Kgf
Oil = medium viscosity

12 pph Latex Addition Level



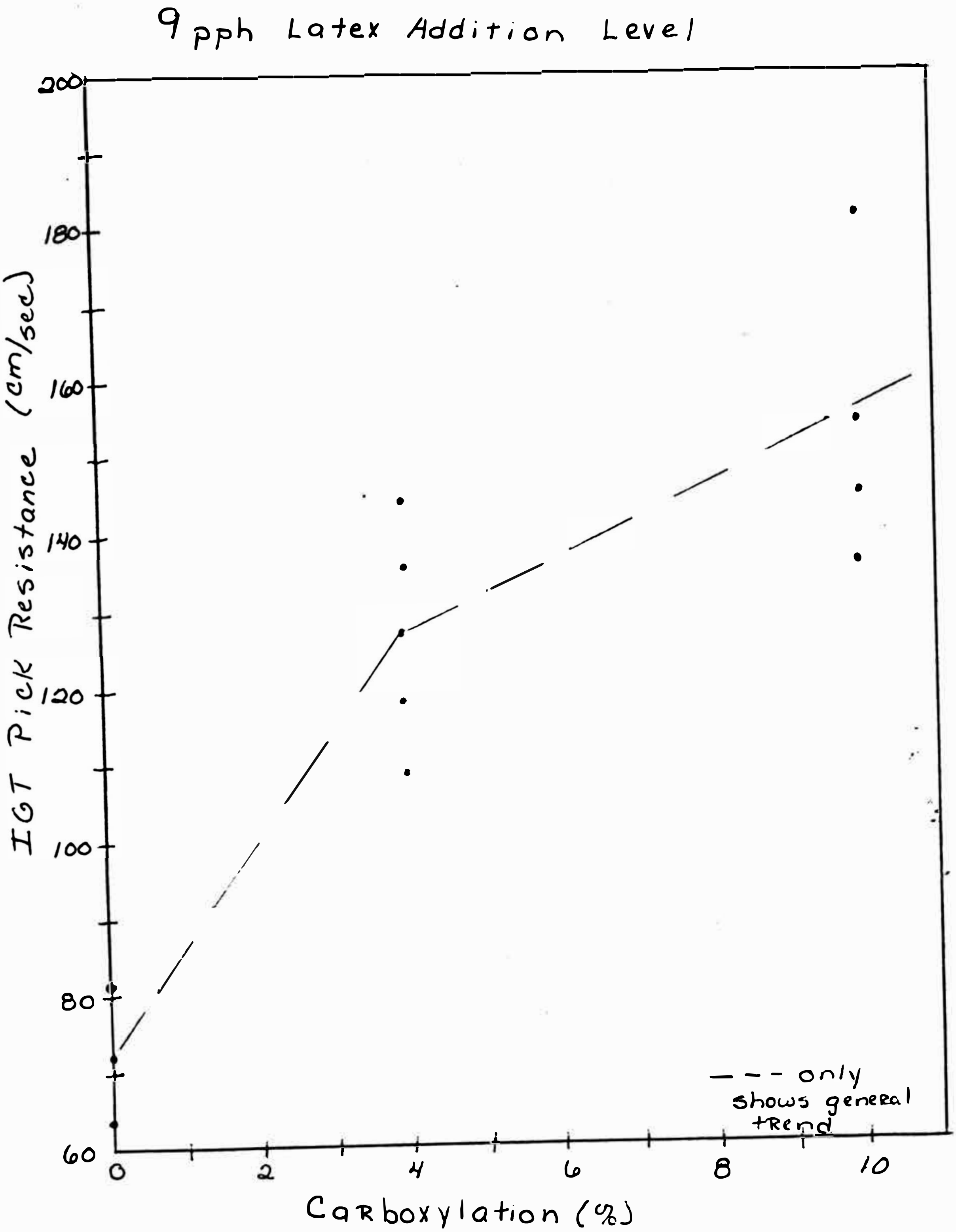
DATA
IGT PICK RESISTANCE
cm/sec

9-0	9-4	9-10
64	109	145
64	127	145
64	127	145
82	118	136
64	127	145
73	127	136
73	127	154
82	118	182
64	145	145
73	127	136
64	118	145
64	127	145
73	127	154
64	118	145
64	145	136
73	118	136
64	127	145
64	127	145
73	118	136
82	145	182
64	118	136
73	127	154
64	109	136
73	127	145
64	136	145
64	136	154
64	127	145
64	127	145
64	127	145
73	118	145
73	109	154
82	127	145
64	127	154
64	136	145

DATA
IGT PICK RESISTANCE
cm/sec

9-0	9-4	9-10
73	127	136
82	118	145
73	127	145
64	127	154
64	118	145
73	127	145
64	127	136
64	127	136
73	118	154
82	109	145
82	118	145
64	127	145
64	127	145
73	136	136
73	118	145
64	145	154
64	145	154
82	118	145
64	127	136
64	136	145
73	118	145
64	118	154
64	127	145
73	127	145
73	118	136
64	127	145

Speed = 2.0 m/sec
Force = 45 Kgf
Oil = low viscosity


9 pph Latex Addition Level
IGT Pick Resistance (cm/sec)
200
180
160
140
120
100
80
60
0
2
4
6
8
10
Carboxylation (%)
--- only shows general trend

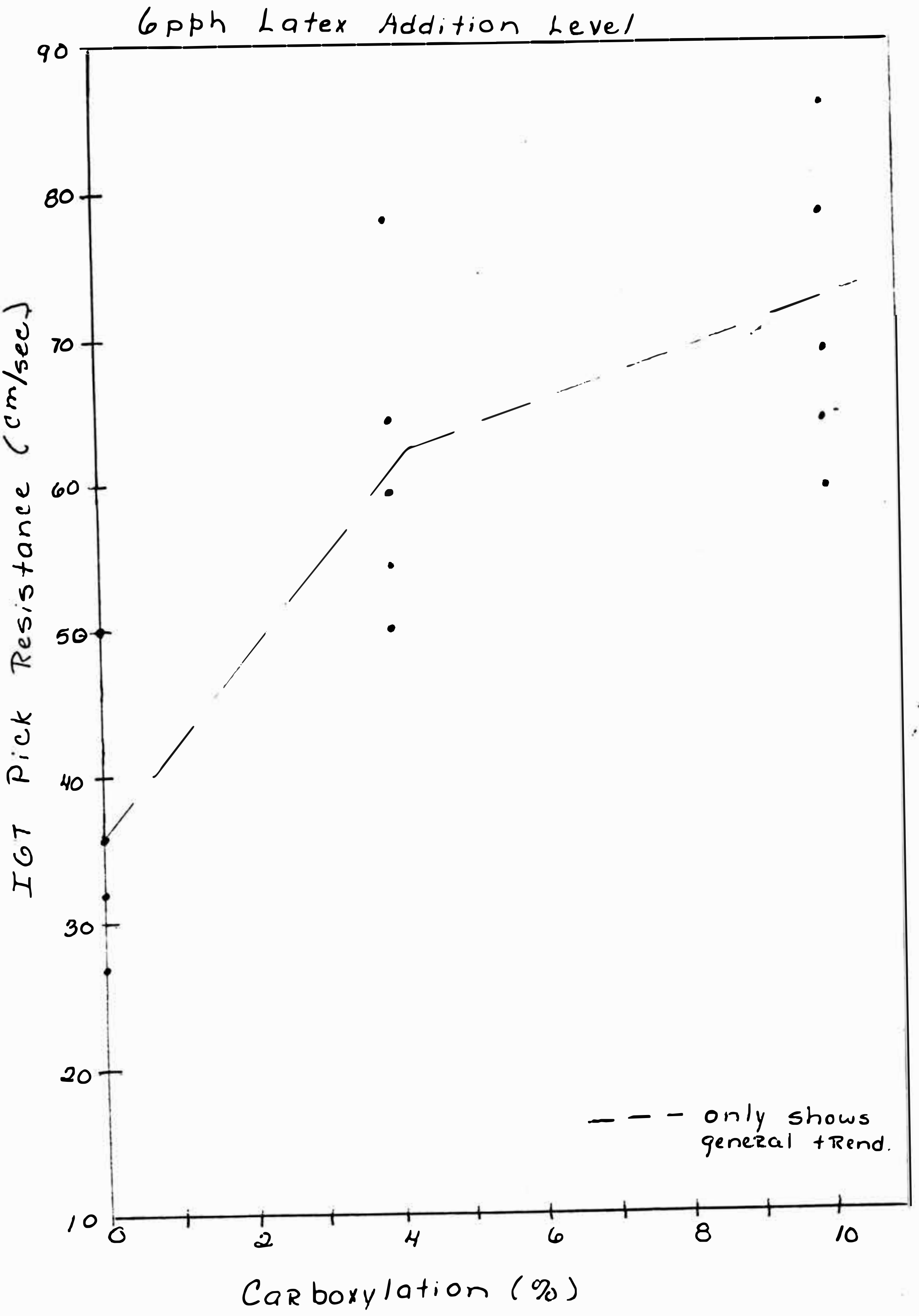
. DATA
IGT PICK RESISTANCE
cm/sec

6-0	6-4	6-10
27	54	68
27	54	64
27	64	64
32	59	68
27	54	86
32	50	64
32	59	64
50	54	68
32	54	77
27	54	68
27	54	68
27	54	64
32	50	64
32	50	68
27	59	77
27	64	77
27	64	68
32	50	68
27	59	77
27	50	77
32	50	86
27	54	77
27	59	77
32	54	86
32	50	77
32	50	64
27	59	77
27	77	77
27	50	77
32	59	68
27	54	64
32	54	59
27	59	59
27	50	68

DATA
IGT PICK RESISTANCE
cm/sec

6-0	6-4	6-10
36	59	77
32	50	68
32	54	68
32	50	77
36	50	68
32	54	68
27	50	68
27	50	86
27	54	68
36	54	68
27	54	77
27	50	77
32	54	64
32	50	64
27	59	77
27	64	64
32	59	77
32	50	77
27	54	68
50	54	86
32	59	77
32	54	64
27	54	77
32	50	77
27	59	64
27	54	68

Speed = 1.0 m/sec
Force = 35 Kgf
Oil = low viscosity


6pph Latex Addition Level
IGT Pick Resistance (cm/sec)
90
80
70
60
50
40
30
20
10
0
2
4
6
8
10
Carboxylation (%)
- - - only shows
general trend.