Ref #3

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DESOTO'S 2898 - HOT TINT COMPATIBILITY

The following data and speculations are based on the writer's examination of Dow and Rohm & Haas literature on acrylic emulsion paints.

It is quite apparent that methocel is widely used as a viscosity control agent, and that it could be the major cause of our difficulties with "Hot" tint compatibility.

R. Pascal has reported that RW-768-P was successfully used at DeSoto when the formulation was changed from methyl cellulose to hydroxyethyl cellulose, a more water soluble type. Pascal has also reported that three systems (DeSoto's, Dow's 2647 and Rohm & Haas' Rhoplex AC-34) containing methyl cellulose all show hot tint sensitivity.

To definitely pin this point down, I have requested an experimental emulsion from DeSoto without methocel for test. If we could obtain this, a rigorous understanding of the problem would be at hand.

A discussion of this general matter of emulsion formulation with F & F would be of considerable help. It is my understanding that they do not use methyl cellulose. It would be interesting to know why not.

J Jackson

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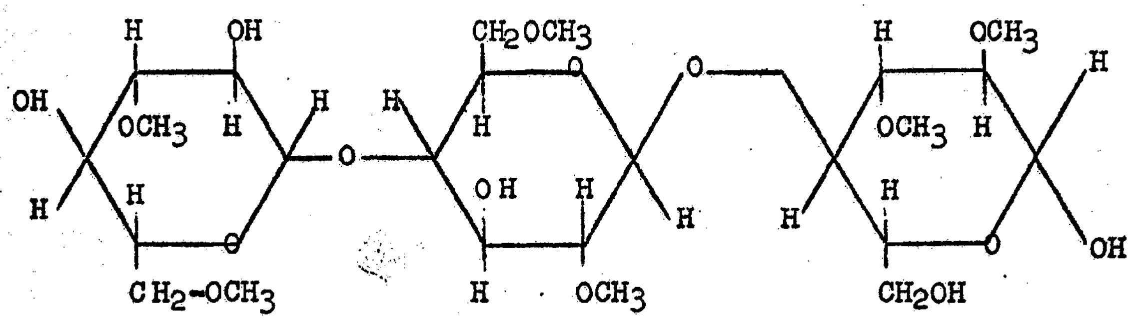
JJ:dm
Attachment

N39901

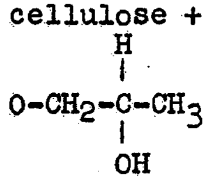
FROM METHOCEL - DOW CHEMICAL LITERATURE

Chemistry:

1. Polymer methyl cellulose



made from cellulose + NaOH + methyl chloride; also



substitution available
propylene glycol ether of cellulose

2. Vary in number substituted OH groups which determine solubility - viscosity, etc.

Solution:

Methocel is a nonionic hydrophilic polymer which forms aqueous dispersion by swelling and successive hydration of structural layers. No distinct solubility limit occurs. The degree of hydration is adversely effected by temperature. This dehydration lowers the viscosity level of a given methocel suspension i.e., viscosity drops with increase in temperature.*

Direct cold water dispersibility of methocel products is assisted by the addition of approximately 2% (based on methocel) of wetting agents such as Witco's #912 and Dowfax 9N10.

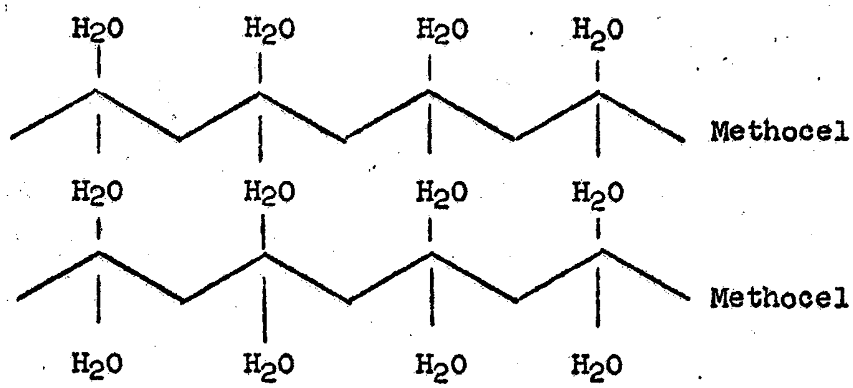
Thermal Gelation:

Thermal gelation is one of the unique properties of methocel i.e., the tendency of the methocel in dispersion to gel on heating (result of dehydration of the outer layers of polymer).

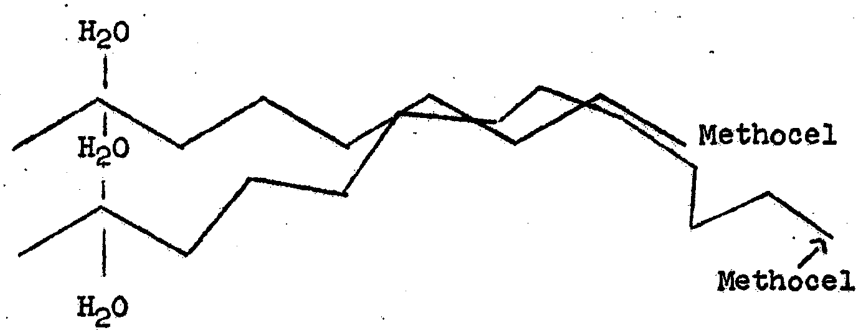
*Note: Tests made on DeSoto's #2898 whitebase indicate that its viscosity is lowered substantially by heating it to 120°F.

DISPERSION

(Swelled structure separated by water. H_2O acts as lubricant)



GEL STRUCTURE



Dehydration results in lack of lubrication between layers and subsequent gelation.

The addition of salts and other additives depresses the thermal gel temperature. Effectiveness is a function of valency, high valence being more effective.

The gelation phenomenon is thermally reversible on cooling. Addition of ethanol or propylene glycol raises the gelation temperature. Armac* Armac HDT* Hyamine 1622, urea also reported to raise the gelation temperature.

ADDITIVES

Methocel is a nonionic and, therefore, not precipitated by metal ions.

* Dow's pamphlet is in error here, since these are not correct designations for Armour's Armac series of products.

Dow recommends the following defoamers:

a. Foamicide 581B - Colloids, Inc.
b. Antifoam A, AF, B, C, - Dow
c. Nopco KFS
d. Nopco NXZ
e. Lauryl alcohol, tri-n-butylphosphate, poly glycol 1200, 2000.
f. Latex paint system - Nopco NDW
g. Polyvinyl acetate - Nopco 1497
h. Acrylic systems - Nopco JMK
i. Styrene Butadiene - Nopco JMK

25 - 1000 PPM (solution weight basis)

VISCOSITY STABILITY

1. Numerous agents added to Methocel dispersion have anomalous effects on the viscosity.

		Increase
Anionics RWA 50	Monobutyl phenyl phenol	+ 60%
300	sodium monosulfonates	140%
375	Robert's Chemical Company	4500%
100		14000%
Dowicide B		8%
F	Dow Chemical	400%
G		58000

pH range 3-11 has little effect on viscosity stability in storage. Solutions in strong acid or alkali will show decreased viscosity on storage.

METHOCEL - UTILITY IN LATEX AND EMULSION PAINTS

In addition to viscosity control, methocel addition to various latex and emulsion paints results in

1. better package stability
2. better application properties (thixotropy effects)
3. good color and wash resistant characteristics

Methocel 65HG and 90HG types are widely used.

The writer is speculating that the weak tints resulting from the "Hot" tinting of DeSoto's #2898 and other systems may be due to some temperature reversible phenomena such as the gelation referred to in the previous section which results in lowered viscosity and possibly decreased dispersion of the blue concentrate. This may be further complicated by the specific interactions of the surfactants, and other components of the blue or green dispersion on the methocel dispersion.

The function of the very high amount of surfactants found in the Hilton-Davis products may be two-fold: (a) a portion to obtain a good color dispersion; (b) a portion to keep the methocel containing white base undisturbed (not gelled etc.) on addition of the color concentrate.

Our experience to date with Witco's #912 seems to bear this out since it is known that this agent aids in the disolution of methocel. Other materials such as Dowicide G, Propylen Glycols etc., which are known to raise the gelation point of methocel will be tested. NG

DOW'S ACRYLIC EMULSION SYSTEMS - GENERAL AGENTS USED

Dow's recommendations include:

AGENT	PROBABLE FUNCTION
ethylene glycol, Poly glycol 1200 defoamer	wetter for Methocel?
Dowfax 9N10, 9N9	wetter for methocel, Pigment.
Methocel 65-HG 4000	thickener
Hydroxyethyl cellulose cpc.	thickener
Colloid 707PS, Nopco 1497, Nopco NXZ defoamers	(Colloid Inc., Nopco Chemical)
PMO-30	Preservative (Troy Chemical).
Potassium Tripolyphosphate	Pigment dispersant
Tamol 731	Pigment dispersant
Daxad 30	Pigment dispersant
nonionic wetting agent Emcol 5138	Witco?

Usual pH 8.5-9.0

Problems of color acceptance are referred to. Additional wetting agents (alkanolamine condensates, alkyl phenyl-ethylene oxide condensates) are recommended.

RHOPLEX ACRYLIC EMULSIONS - GENERAL AGENTS USED

Rohm and Haas literature refers to the use of:

AGENTS	PROBABLE FUNCTION
Hydroxyoctyl cellulose	
Methyl cellulose	thickeners.
Tamol 731	Pigment Dispersant
Triton CF10	Pigment Dispersant
Tamol 850	Pigment Dispersant
Balab 748, Nopco 1497, Nopco NXZ	Antifoams
Ethylene glycol	(Methocel Dispersant?) defoamer.

pH 9.0

REFERENCE #6

VI. AQUEOUS DISPERSIONS

A. BW-431-P - Role of Structure of Surfactants (JJ)

The role of the structure of surfactant and quantitiy used on the dispersion of BT-352-P has received considerable attention. An accelerated making procedure based on the use of a Jiffy-Mill has been developed and gives fairly reproducible results.

Evaluation

Table I lists some of the tests made and results achieved in casein brushout. Siponic E15 and Pluronic F68 are superior to Renex 20, our presently used agent in this application.

Examination of these dispersions in DeSoto's acrylic emulsion system indicated that the strength advantages noted in casein are carried through (See Table II). However, all of these pigment dispersions fail the so called "Hot Tint" test (weaker when tinted at 120°F. then when tinted at 80°F.). The phenomenon appears to involve a flocculation of the blue since it can be "rubbed up" to standard strength. In most cases this is a reversible phenomenon i.e. the weak tint comes back to standard strength on cooling.

The basic cause of this situation seems to involve the Methocel used as a viscosity controlling agent in the DeSoto system. We are trying to prove this by requesting Methocel-free vehicle from the manufacturer.

The addition of Witco #912, a proprietary mixture of anionic and nonionic type agents, to either a Renex or Siponic E15 system, reduces the hot tint sensitivity. The use of this agent, to assist methocel solution,is known to the trade.

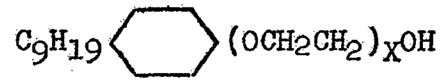
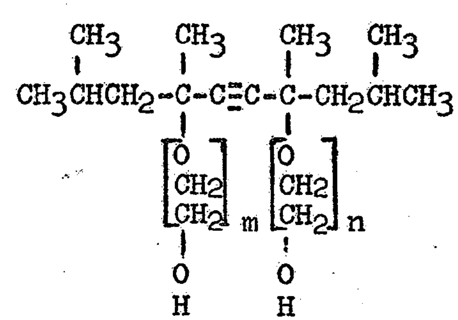
Dispersions using mixtures of Siponic E15 and Witco #912 show decreased levels of foam, good hot tint dispersibility but lower strength levels than desired. This approach is receiving further attention.

TABLE I

ROLE OF SURFACTANTS ON CONVERSION OF BP-352-P TO BW-431-P

NB #	Agent	% CPC Amt.	HLB	Casein Brushout Res. vs. BW-431-P	STRUCTURE
108-1E	Renex 20	25-37	13.8	1-2% stronger	POE ester fatty and rosin acids.
108-17	Renex 30	25	14.5	7-10% weak	polyoxyethylene ether-alcohol
	Renex 31	25	15.4	7-10% weak	polyoxyethylene ether-alcohol
	Renex 36	25	11.4	7-10% weak	polyoxyethylene ether-alcohol
	Structure more important than HLB				
108-3	Siponic L1	25		extremely wk	Lauryl alcohol plus increasing amounts ethylene oxide.
	Siponic L12	25		7-10% weak	
	Siponic L25	25		1-2% stronger	
	Sufficient ethylene oxidefor water dispersibility essential				
108-3	Siponic Y050	25		extremely wk	Oleyl alcohol plus increasing amounts of ethylene oxide.
	Siponic Y100	25		2% weak	
108-17	Siponic Y150	25		2-3% strong	Oleyl alcohol plus increasing amounts of ethylene oxide.
	Siponic Y500	25		2-3% strong	
	Siponic Y503	25		3-4% strong	
	Sufficient ethylene oxide for water dispersibility essential.				
108-3	Siponic E3	25	10.1	3-4% weak	stearyl-cetyl alcohol plus increasing amounts of ethylene oxide.
	Siponic E4	25	11.5	5% strong	
108-13G	Siponic E5	25		7-10% strong	Ditto
108-13H	Siponic E10	25		5% strong	
108-13I	Siponic E15	25		5-10% strong	
108-13J	Siponic E20	25		5-10% strong	

Chain length and type of alkyl group coupled with sufficient ethylene oxide amount are both highly important. E15 seem optimum. Foaming increases with increased POE content.

NB #	Agent	% CPC Amt.	HLB	Casein Brushout Res. vs. BW-431-P	STRUCTURE
108-5	Polytergent				
	J-200	25		10% weak	$C_{13}H_{27}(OCH_2CH_2)_5OH$
	J-500	25		3-5% weak	$C_{13}H_{27}(OCH_2CH_2)_{15}OH$
	Chain length and type of alkyl leg very important				
108-5,7	MYRJ45	25	11.1	3-5% weak	polyoxyethylene stearate
	MYRJ59	25	18.8	Ca=	polyoxyethylene stearate
108-5	Igepal W710	25		5-10% weak	
	Igepal W530	25		5-10% weak	ibid - less POE
108-5	EthoMeen C/25	25		Ca=	$R-N<\begin{matrix}(CH_2CH_2O)_xH \\ (CH_2CH_2O)_yH\end{matrix}$ (Coco amine)
108-7	EthoMeen 18/60	25		4% weak	$R-N<\begin{matrix}(CH_2CH_2O)_xH \\ (CH_2CH_2O)_yH\end{matrix}$ (steary amine)
108-7	Ethomid HT-60	25-37		4-6% wk, 2% strong	$R-\overset{O}{\overset{\parallel}{C}}-N<\begin{matrix}(CH_2CH_2O)_xH \\ (CH_2CH_2O)_yH\end{matrix}$ (Halogenated Tall Oil)
108-7	Ethofat 242/15	25		3-5% weak	$R-\overset{O}{\overset{\parallel}{C}}-O(CH_2CH_2O)_xH$
108-7	242/60	25		3% weak	Ibid - more POE
108-13	Surfynol 470	25		2 weak	
	TG	25		2 weak	

NB #	Agent	% CPC Amt.	HLB	Casein Brushout Res. vs. BW-431-P	STRUCTURE
108-21	Pluronic F38	25		1-2% strong	$HO(CH_2CH_2O)_a-(CH(CH_3)CH_2O)_b-(CH_2CH_2O)_cH$
	Pluronic F68	25		3% strong	
	Pluronic F88	25		5% strong	

Pluronic F88 seems to be better than Renex 20 but on defensive versus Siponic E15. Should be considered however.

NB #	Agent	% CPC Amt.	HLB	Casein Brushout Res. vs. BW-431-P	STRUCTURE
108-27	Jefferson LF6	38.4		v weak	aliphatic alcohol ethylene oxide adducts
	Jefferson LF7	38.4		v weak	"Low Foam".

TABLE II

DESOTO ACRYLIC EMULSION #2898 COMPATIBILITY HOT VERSUS COLD TINT[1]

	SAA	% SAA on CPC	Structure Agent	Results	Effect vs C#
Seatone Phthalo Blue		75	unknown, nonionic?	sl wk vs rd	Control
BW-431-P	Renex 20	25	POE ester of fatty and rosin acids	v wk	much ws
108-3F	Siponic E4	25	ethoxylated lauryl alcohol	v wk	much ws
108-13B	Siponic E4	24	no dowicides	v wk	much ws
108-20E	Siponic E15	25	ethoxylated stearyl-cetyl	ext wk	v much ws
108-20E	Add Witco #912	2	anionic-nonionic	vvsl wk	better than E or C#
108-20E	Add butycellosolve			ext wk	vm ws - no improvement vs.E
108-21C	Pluronic F68	25	polymer-POE; polyoxy isopropyl alcohol	ext wk	ws than C#
108-24B	Siponic E15	38	anionic	ext wk	ws than C#
108-24B	Blancol	3.8	anionic	ext wk	ws than C#
108-30D	Witco #912		anionic-nonionic mixture	wk	ws than C#
108-20C	Renex 20		Ibid	v wk	ws than C#
108-20C	Add Witco #912		Ibid	vvs wk	bet than C#

	SAA	% SAA on CPC	Structure Agent	Results	Effect vs C#
108-17E	Renex 30	25	POE ether-alcohol	v wk	ws than C#
108-17F	Renex 31	25	POE ether-alcohol	vv wk	ws than C#
108-17G	Renex 36	25	POE ether-alcohol	v wk	ws than C#
108-30F	[3,4] Siponic E15	11.5	POE ether-alcohol	vs wk	bet than C#
108-30F	[3,4] Witch #912	26.9	POE ether-alcohol	vs wk	bet than C#

1 Hot tint is weak - mechanism seems to be flocculation rubbed portion becoming stronger (like cold tint). If tint allowed to stand sufficient time usually reverts to cold tint strength level.

2 Effect proportional to amount Witco #912 added. Witco #912 added to previously prepared dispersion of blue.

3 Attempt to prepare dispersion by co-jiffy-milling with Siponic E15/Witco #912.

4 Ultimate strength not up to C#.

REFERENCE #7

VI. AQUEOUS DISPERSIONS

A. BW-461-P - Increased Strength (JJ AND RFW)

Work has been contined on the modification of the BT-352-P route to an improved blue dispersion for DeSoto Paint. Emphasis has been placed on:

1. Development of optimum size reduction method and isolation techniques for making BT-352-P.

2. Development of optimum conditions for converting a high strength BT-352-P to an aqueous dispersion.

A stronger BT-352-P (Lot 31308) has been produced by grinding the CPC crude with a higher Blancol ratio (15% vs. 10% toner basis) and an increased power input (45 vs. 25 Amps.), following Shriver washing to 7000 ohms and thickening to a solid of 25% instead of the conventional acid extraction and Diphenyl Quanidine flocculation. This product was then made into an aqueous dispersion utilizing 50% of Emulphor EL-620. The product tested out satisfactorily versus Hilton-Davis Super Seatone Phthalo Blue in DeSoto Acrylic finish, and DuPont's "Lucite" and "Flowkote". Samples have been submitted to DeSoto Paint and F & F for evaluation. Experimental studies leading to this result are tabulated on the next page.

NB 108-31 - Study of MYRJ-59 (polyoxyethylene stearate); Ethomeen C-25 (ethoxylated coco amine); Ethomid HT-60 (hydrogenated tallow oil); Ethofat 242-60 (ethoxylated fatty acid); Ethofat 242-25 (ethoxylated fatty acid, higher POE).

None of these surfactants was satisfactory in strength or hot tint compatibility.

NB 108-32 - Study of Siponic E-15 (ethoxylated steary - cetyl alcohol) Renex 20 (POE ester of fatty and resin acids); Sinclair 1440H (esterfied styrene - maleic anhydride copolymer); Dowfax 9N10 (ethoxylated nonyl phenol).

A specially milled BT-352-P (29809) was used. None of the products were adequately strong. All were poorer in hot tint compatibility.

NB 108-33, 34, 35 - Study of Siponic E-15, Renex 20

Utilizing specially milled (104-13E) BT-352-P (high energy milled Shriver thickened) products exhibited adequate strength to the competitive, but were inadequate in hot tint compatibility. Addition of Defoamer, Nopco Chemical's Nopco L, NXZ, and NOW had little effect on strength and marked effects on foam reduction. Addition of Witco's #912 agent to white tint base prior to addition of blue will correct hot tint compatibility.

NB 108-36 - Continuation of Studies on High Energy Milled BT-352-P Utilizing Renex 20 and Lipal 30W (ethoxylated vegetable oil).

Cold tint strength was fairly close to the C#, Lipal 30W showed some improvement in hot tint compatibility versus standard agent, Renex 20.

NB 108-37, 40 - Continuation of Studies using High Energy Milled BT-352-P Coupled with Siponic E-15, E-4 and E-15 Mixtures and a New Surfactant Emulphor EL-620 (ethoxylated castor oil).

Strength was inadequate. Hot tint compatibility was very good when the latter agent was used at 25% toner basis. Increasing surfactant level to 50% gave rise to an excellent product.

NB 108-39 - Continuation of Studies of Surfactants - Surfonic 16 & 17 (Structures Not Known Exactly) and Adsee 85 (polyoxy ethylene thio Ether)

None of these were adequate in hot strength compatibility.

NB 108-43

108-40D was scaled up through homogenizer. Products were obtained which were stronger than the competitive and satisfactory in hot tint compatibility.

NB 108-49

Various lots of Emulphor EL-620 were tested for uniformity of effect in DeSoto's vehicle. All worked satisfactorily.

NB 108-57

Tests were made in Mobile Paints acrylic (known to contain Methocel) to compare standard BW-431-P, Hilton-Davis Super Seatone, and experimental 108-43 type. The latter product was again for superior to BW-431-P and satisfactory versus the competitive.

NB 108-53, 55

108-43 type was scaled up successfully in the plant (BT-352-P - Lot 31308).

NB 108-54

A study was made of other so called ethoxylated castor oils (Atlas G-1292, G-1295, G-1300). Some strength advantage over Emulphor EL-620 was shown but hot tint compatibility in DeSoto vehicle was inadequate.

Red Shade Aqueous Dispersion

Studies were undertaken to develop a red shade dispersed paste. These are summarized below.

NB 108-41

N-623 (solvent milled Blue LB) was Jiffy milled with 35% Emulphor EL-620. Products were weaker and duller than Harmon's Super Seatone Phthalo Blue and satisfactory in hot tint compatibility.

NB 108-45, 47

Attempts to utilize Orchem's acid pasted LB type pigment to develop a red shade product was unsatisfactory. Emulphor EL-620 was used to make the dispersion.

NB 108-48, 52

Attempts were made to use N-872 (acid swelled Blue R paste) to develop a strong red shade paste. Emulphor EL-620 dispersions gave interesting strong red shade products, exhibiting good hot tint compatibility in the DeSoto vehicle. This process deserves further study. Siponic E-15 gave a dispersion exhibiting higher strength in Casein type dispersions.

The use of acid swelled Blue R looks very interesting and will receive more study.

Stronger GW-749-P

Studies were undertaken to develop a stronger GW-749-P utilizing the same approaches that lead to BW-461-P. These are summarized below.

NB 108-42

Comparisons were made of

Daxad 11
Siponic E-4
Siponic E-15
Renex 20
Emulphor EL-620
Emulphor EL-720 (more POE)

utilizing a common GT-735-P (standard quality lot). Optimum strength levels and compatibility was achieved via the Emulphor EL-620 approach.

NB 108-44

An attempt was made to increase the strength of GT-735-P by lowering the temperature of the standard acid extraction, and by eliminating the DPG flocculation. Products were obtained via Emulphor EL-620 use which were slightly stronger than standard GW-749-P.

NB 108-46

Various isolation techniques were studied to isolate a smaller particle size GT-735-P from a special high energy milling. These compared

1. Standard acid extraction and DPG flocculation 195°F.

2. DPG flocculation 150°F.

3. ODCB and $Al_2(SO_4)_3$ 18 H_2O flocculation 150°F.

Route #2 gave the best result (sl stronger than standard acid extraction and DPG flocculation) but inadequate to match the Harmon Super Seatone Phthalo Green.

NB 108-50

Continuation of low temperature DPG flocculation (80°F.). Products obtained stronger than GW-749-P but not equivalent to competitive.

NB 108-56

Laboratory studies of HF milling initiated. This was a control run using Blancol. Standard strength level GW-749-P was achieved.

NB 108-57

A study of the E. T. Oaks Corporation's pulverizer as a possible substitue for the homogenizer, showed that equivalent results were achieved.

NB 108-58, 61, 64

Attempts to HF mill with Polyfon T in the laboratory gave rise to stronger GW-749-P than that resulting from use of Blancol. Scale up in larger milling units is indicated. Products close to the competitive in strength have been achieved.

NB 108-59, 60D

Purification via acid extraction, of N-770 seems to indicate the possibility of achieving a higher strength GW-749-P via higher CPC purity. Should be coupled with best plant grinding conditions, if necessary.

NB 108-60, 64

HF milling with Lomar D gave rise to relative small particle sized GT-735-P in the milling (as judged by particle size index) but the products after isolation via feasible methods were not as strong as those made with Polyfon T or higher amounts of Blancol.

NB 108-63

Specially milled GT-735-P (higher energy input coupled with increased Blancol, ex plant milling, Shriver washed and thickened) was converted to dispersed pastes in the laboratory using Emulphor EL-620. The products are stronger than GW-749-P but are not quite as strong or intense as the competitive. Hot tint compatibility seems to be satisfactory.

NB 108-62

Study of high ratios of Blancol gave rise to stronger GW-749-P, after modification of the extraction procedure.

Both Polyfon T and high blancol type millings look interesting and will be studied further. The use of purified crude N-770 is also deserving of further study.