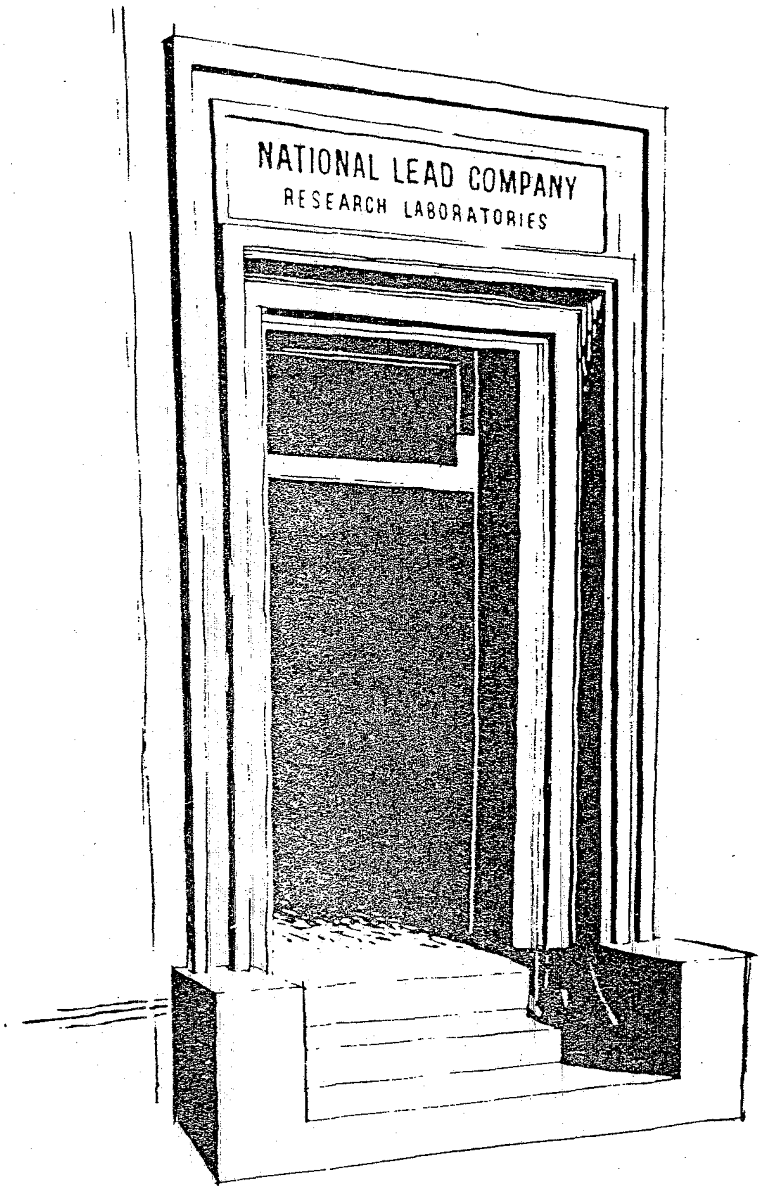
Dutch Boy®

Handbook on

STABILIZERS for VINYL RESINS



NATIONAL LEAD COMPANY

NATIONAL LEAD COMPANY

DATA SHEET BG-1

LATEX EMULSION PAINTS

"DUTCH BOY" BEN-A-GEL is a highly efficient inorganic, insoluble thickening agent for latex and emulsion paints. It is ideally suited for use in styrene-butadiene, acrylic, and polyvinyl acetate emulsions for imparting a thixotropic viscosity increase. This type of body is especially advantageous in low solids content paints to obtain a good working viscosity, easy brushing, and sag control.

BEN-A-GEL is insoluble in water and is not sensitive to spotting or staining by water. This property recommends it particularly for thickening acrylic and polyvinyl acetate latex paints, as an excellent way of avoiding water spotting and streaking of the dried film.

When BEN-A-GEL is properly dispersed in a latex paint, it is present as millions of tiny platelets less than one micron in size. The distribution of so many tiny flakes provides measurable reinforcement for the dried film, as shown in improved scrub resistance and stain removal tests.

BEN-A-GEL greatly aids the dispersion of poor wetting inorganic and organic color pigments. The wetting action of the gel coating markedly reduces pigment streaking, floating, agglomeration, and settling. BEN-A-GEL also provides more complete color development with these poor wetting pigments in pastel colored paints.

The inorganic, insoluble BEN-A-GEL structure acts as a protective colloid in mechanically stabilizing latex emulsion paints. The emulsion and viscosity stability of paints are greatly improved by the use of BEN-A-GEL. Since its gelling action is not a function of solubility, changing temperatures have no effect on BEN-A-GEL's gel structure. This outstanding property is extremely advantageous when emulsion paints are exposed to freeze-thaw conditions. ?

BEN-A-GEL dispersions in water have a pH of about 8.0 to 8.5. However, it will gel efficiently in solutions ranging from pH 5.0 to 10.0. Its buffering action minimizes the usual pH drift encountered during the aging of latex emulsion paints. Being entirely inorganic, BEN-A-GEL is not subject to oxidation nor microbiological degradation. As a result, less fungicides are required in paints containing it. This is a decided asset, since these agents generally detract from the moisture resistance of the dried paint film.

The general recommendation for BEN-A-GEL in latex emulsion paints is 2 to 4 lbs. per 100 gallons of finished paint. It may be incorporated into a paint in either of two ways. Whenever possible, it is best to incorporate dry BEN-A-GEL directly into the pigment grind, mixing the dry powder thoroughly into the pigment paste before milling. In some cases, it may be advisable to use a 3 to 4% masterbatch of BEN-A-GEL in water, which has been prepared separately using an homogenizer or colloid mill. Whenever only high speed stirring is available, it is recommended that BEN-A-GEL be wetted with an equal weight of a glycol, such as diethylene glycol, propylene glycol, or glycerol, prior to its dispersion in water. The glycol additive aids the gelling of BEN-A-GEL, which will approach the efficiency of higher shear dispersion. The masterbatch gel may be added either to the pigment grind or immediately afterwards, when the pigment and vehicle are blended.

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The following primer-sealer and tint base formulations for styrene-butadiene, acrylic, and polyvinyl acetate latex emulsinn paints serve as excellent guides to an inveitgation of the many advantageous properties of BEN-A-GEL.

STYRENE-BUTADIENE PRIMER-SEALER

Grinding Base	Pounds	Gallons
TITANOX RA	58.0	1.56
China Clay	58.0	2.68
Mica, 325 mesh	77.0	3.27
Potassium Tripolyphosphate	0.73	0.04
BEN-A-GEL	3.0	0.15
Water	142.0	17.04
Let-Down		
Dow 512K or 762W (48% solids)	530.0	63.00
Cascoloid ST-40 (15% casein solution)	102.0	11.70
Dowicides 1 and 7 (1:1 50% in Dowanol)	9.7	1.22
Nopco Defoamer 1407	1.5	0.17
Ammonium Hydroxide (28%)	(adjust to pH 9.5)	
	981.93	100.83

wt./gal. = 9.7 lbs.

STYRENE-BUTADIENE TINT BASE

Grinding Base	Pounds	Gallons
TITANOX RA	175.0	5.00
LORITE	100.0	4.71
Celite 281	25.0	1.30
China Clay	50.0	2.31
Potassium Tripolyphosphate	1.5	0.07
BEN-A-GEL	3.0	0.15
Water	267.0	32.04
Let-Down		
Dow 512K or 762W (48% solids)	340.0	40.40
Cascoloid ST-40 (15% casein solution)	75.0	8.63
Dowicides 1 and 7 (1:1 50% in Dowanol)	11.0	1.38
Nopco Defoamer 1407	1.5	0.17
Ammonium Hydroxide (28%)	(adjust to ph 9.5)	
	1049.0	96.16

wt./gal. = 10.9 lbs.

ACRYLIC PRIMER-SEALER

Grinding Base	Pounds	Gallons
TITANOX RA	59.0	1.69
LORITE	182.0	8.38
Calcium Carbonate	182.0	8.10
Tamol 731 (10% solution)	7.7	0.92
Acrysol A-3 (10% ammonium salt in water)	7.7	0.96
Tributyl Phosphate	7.1	0.87
Pine Oil	2.4	0.31
Boric Acid	5.7	0.48
Napco Defoamer 1407	2.2	0.25
BEN-A-GEL	3.0	0.15
Water	177.3	21.28
Let-Down		
Rhoplex AC-33 (46% solids)	362.0	41.70
Water	142.0	17.04
Ammonium Hydroxide (28%)	(adjust to	pH 9.0)
	1140.1	102.13

wt./gal. = 11.2 lbs.

ACRYLIC TINT BASE

Grinding Base	Pounds	Gallons
TITANOX RA	213.7	6.11
LORITE	228.0	10.73
Tamol 731 (10% solution)	6.5	0.78
Acrysol A-3 (10% ammonium salt in water)	6.5	0.78
Boric Acid	6.3	0.53
Napco Defoamer 1407	2.1	0.25
Diethylene Glycol	8.4	0.99
BEN-A-GEL	3.0	0.15
Water	133.2	15.98
Let-Down		
Rhoplex AC-33 (46% solids)	407.3	46.95
Water	133.2	15.98
Ammonium Hydroxide (28%)	4.3	0.56
	1152.5	99.79

wt./gal. = 11.6 lbs.

POLYVINYL ACETATE PRIMER-SEALER (EXTERNALLY PLASTICIZED)

Grinding Base	Pounds	Gallons
TITANOX RA	102.0	2.91
Mica, waterground	76.5	3.24
Kayphenate OP (1% solution)	10.0	1.20
Foamicide #581B	2.0	0.28
Daxad 23 (1% solution)	2.0	0.24
Ethylene Glycol	85.5	9.20
BEN-A-GEL	3.0	0.15
Water	242.2	29.06
Let-Down		
Vinylite WC-130 (58.5% solids)	330.8	35.35
NL A-10 (Dibutyl Phthalate)	18.9	2.16
Water	134.3	16.12
	1007.2	99.91

wt./gal. = 10.1 lbs.

POLYVINYL ACETATE PRIMER-SEALER (INTERNALLY PLASTICIZED)

Grinding Base	Pounds	Gallons
TITANOX RA	102	2.92
LORITE	103	4.85
Kayphenate OP (1% solution)	10	1.20
Foamicide #581B	2	0.28
Daxad 23 (1% solution)	2	0.24
BEN-A-GEL	3	0.15
Water	428	51.36
Let-Down		
Everflex G (50.8% solids)	509	56.80
	1159	117.80

wt./gal. =9.8 lbs.

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POLYVINYL ACETATE TINT BASE

Grinding Base	Pounds	Gallons
TITANOX RA	158	4.52
LORITE	158	7.45
Kayphenate OP (1% solution)	10	1.20
Napco Defoamer 1407	2	0.22
BEN-A-GEL	3	0.15
Water	430	51.60
Let-Down		
Everflex G (50.8% solids)	453	50.70
	1214	115.84

wt./gal. = 10.5 lbs.

New Products Development
NATIONAL LEAD COMPANY
RESEARCH LABORATORIES
105 York Street
Brooklyn 1, N. Y.
May 28, 1955

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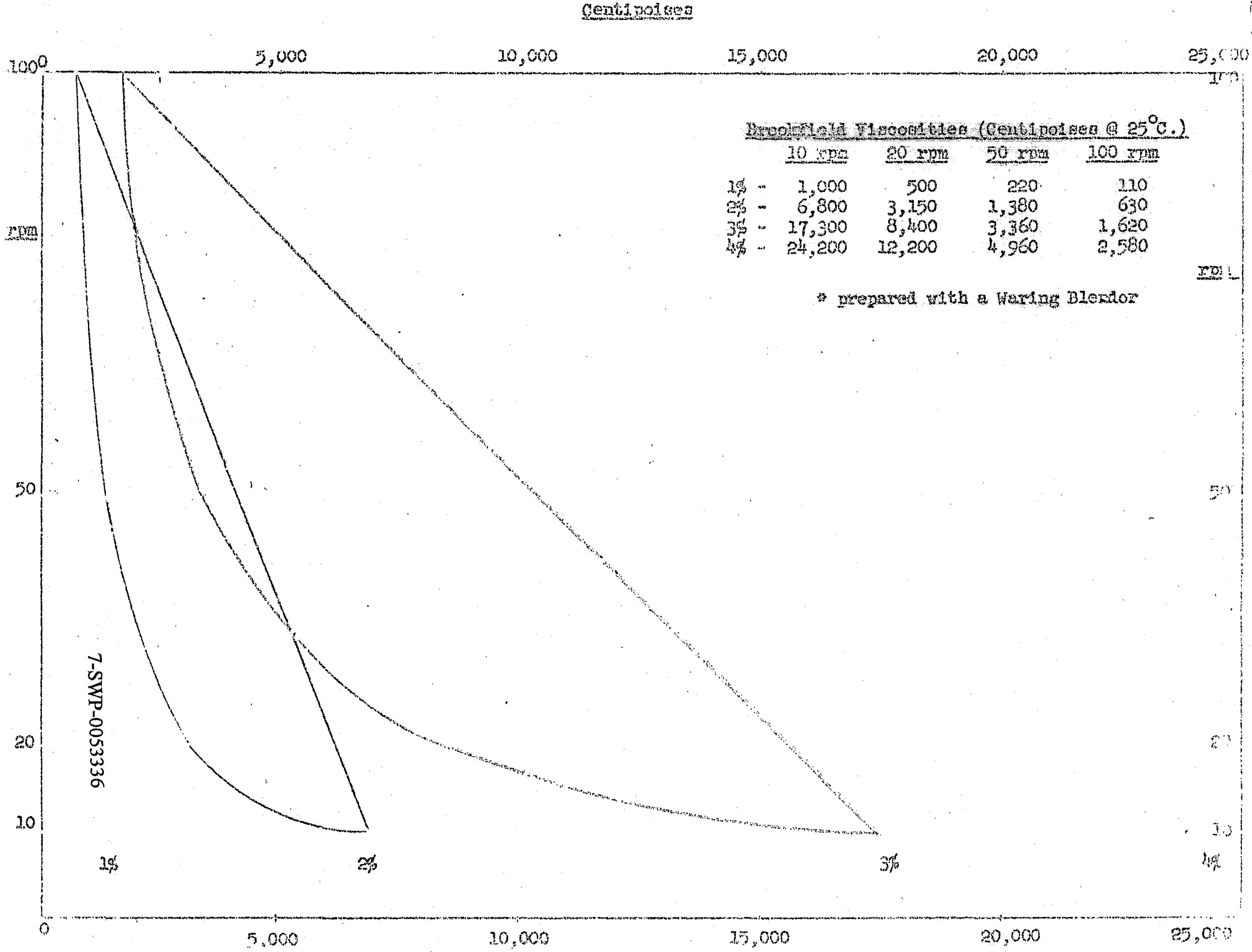

Brookfield Viscosities (Centipoises @ 25°C.)

	10 rpm	20 rpm	50 rpm	100 rpm
1% -	1,000	500	220	110
2% -	6,800	3,150	1,380	630
3% -	17,300	8,400	3,360	1,620
4% -	24,200	12,200	4,960	2,580

* prepared with a Waring Blendor

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FOREWORD

During the past decade, the plastics industry has grown rapidly. That part of the industry consuming vinyl chloride polymers and copolymers has reflected this phenomenal expansion. This has been due in no small measure to the development of materials and techniques for stabilization of vinyl plastics against the harmful effects of heat and light. Such effects, if not counteracted, would promote changes in color and physical properties sufficient to prevent use of vinyl plastics in many desirable applications.

At the time of the publication of our original "DUTCH BOY HANDBOOK FOR VINYL STABILIZERS" in 1949, stabilization was still more or less an "empirical art" rather than a true chemical science. This is no longer the case, because of general improvements in the resins, plasticizers, colorants and stabilizers available to the vinyl plastic industry. These improvements in raw materials coupled with the recognized need for plastic quality commensurate to the times, better compounding, and the application of vinyl plastics only in end-usages where this type of resin is indicated, have brought about a large increase in the production and sales of vinyl resin products. In the ten year period from 1945 to 1955, there has been a four-fold increase in the production and consumption of vinyl chloride resins.

Improvement in stabilizers and stabilizer techniques has kept pace with the volume growth of the industry. We are proud to have played a part in these advancements. The first two editions of the "DUTCH BOY" Stabilizer Handbook emphasized the use of lead compounds. The present edition has been increased in scope, and includes a section on non-lead "DUTCH BOY" stabilizers for applications where lead stabilization is not indicated, such as in clear or highly translucent stocks.

General formulations are given for a wide variety of end applications including practically every type of vinyl product. This expansion of the present handbook reflects 10 years of active field and laboratory experience, and is backed by a most extensive evaluation program of accelerated indoor testing, paralleled by a thorough out-of-door weathering program.* This test program involves the evaluation of resins, plasticizers and stabilizers from all available world sources, kept current in a new and modern plastics research and development laboratory. In addition, the National Lead Company has available complete technical service laboratories, for the application of "DUTCH BOY" vinyl stabilizers and other chemicals in the plastics industry. Your inquiries to our nearest branch office are invited, and technical representatives will be glad to call and discuss individual problems in detail.

*Hendricks, J. G. and White, E. L., *Ind. Eng. Chem.*, 43, 2335 (1951).
Hendricks, J. G. and White, E. L., *Wire and Wire Products*, 27, 1053 (1952).
Hendricks, J. G., *Plastics Technology*, 1, No. 2, 81 (March 1955).

Lead Stabilizers

- DYPHOS®
- DYTHAL®
- DS-207®
- LEADSTAR
- LECTRO "60"
- NORMASAL®
- PLUMB-O-SIL® B
- PLUMB-O-SIL® C
- TRIBASE
- TRIBASE-E

Non-Lead Stabilizers

- CALSTAR
- CLARITE A
- CLARITE B
- CS-137
- FLOMAX 25
- NALZIN
- PROVINITE A
- PROVINITE B

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I. INTRODUCTION

Vinyl chloride was polymerized into resin by Regnault in 1838. However, the commercial development of this resin in the United States did not start for nearly one hundred years. Until 1939, when the industry produced 1.2 million pounds, there was no appreciable volume used. During World War II, the need sprang up for an elastomeric synthetic with good sheeting characteristics and desirable extrudability. Vinyl chloride plastics filled this need admirably, and their use in raincoats, ground cloths, packaging, insulation, tubing, metal coating, and a multitude of similar products important to the armed forces, brought about a hundred-fold growth to the industry between 1940 and 1945.

In 1947, the first genuine post-war year, a rapidly expanding consumer market utilized 150 million pounds of vinyl plastics. The year 1948 brought a further expansion to over 215 million pounds. The present rate of increase indicates an output of between 700 million and 1 billion pounds by 1960.

This rapid expansion may be attributed primarily to the versatility of the thermoplastic vinyl chloride type resins. Modification of the vinyl resins through the use of chemical plasticizers, colorants, and fillers has offered a variety of rigid, semi-rigid and flexible products.

In addition to floor coverings and unbreakable records, uses for flexible plasticized vinyl compounds have been found in belting, upholstery, shoe uppers, luggage, packaging, protective sheets, raincoats, shower curtains, umbrellas, window curtains, garment bags, electrical tapes, electrical insulation, tubing and hose and many other varied products.

The wide range of usefulness makes apparent the necessity of maintaining the original physical properties required for the particular final application. There must be no discoloration or deterioration during the heat processing cycle, shelf life and ultimate consumer use.

This involves the employment of a diversity of raw materials to fulfill specific functions. Certain plasticizers give low temperature flexibility, non-inflammability, "drape," non-migration characteristics, resistance to lacquer lift and any number of further chemical and physical properties. Colorants, fillers and lubricants have been developed which will withstand a variety of processing and service conditions. The multitude of end uses has actually intensified the search for satisfactory component raw materials with which to modify the original vinyl chloride polymer. Even the polymers themselves have been modified by molecular weight variations, and by copolymerization with other materials.

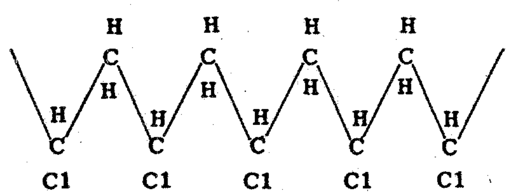
To meet these many and varied present day requirements, a line of "DUTCH BOY" vinyl stabilizers has been developed. These "DUTCH BOY" products not only protect the resins themselves against degradation, but at the same time offer no interference with the other components of a particular vinyl plastic system.

"DUTCH BOY" vinyl stabilizers are also of interest in connection with polyvinylidene chloride, a close relative of the regular vinyl chloride type resins. These stabilizers have considerably improved the light and heat resistivity of this resin.

II. CHEMISTRY OF STABILIZATION

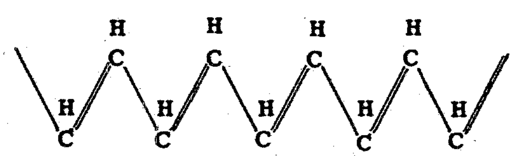
As heretofore indicated, the deleterious action of heat and light encountered during the useful life of a vinyl plastic product promotes changes in color and physical characteristics of the unstabilized vinyl composition which are sufficient to prohibit its use in many otherwise wholly desirable applications. The modes of chemical action whereby such compositions are degraded or may be stabilized must be considered in order to intelligently attack the problem of correctly formulating stable vinyl chloride resin compositions. For present purposes, it will be sufficient to define the resinous vinyl materials herein treated as polyvinyl chloride, with the understanding that this designation includes the polymer of vinyl chloride and the copolymers of vinyl chloride with a lesser proportion of some other monofunctional unsaturated compound, i.e., vinyl acetate, vinylidene chloride, ethyl maleate, ethyl fumarate, etc.

X-ray studies and chemical analysis have demonstrated the structure of polyvinyl chloride to be:



A. HEAT DEGRADATION

It is known that heating polyvinyl chloride resin at temperatures of 80° C. and upward will produce a series of color changes. This reaction gives rise to first a light yellow color, which quickly changes to dark yellow, to orange, and finally to a reddish brown which may ultimately become a charred black. The isolation of hydrogen chloride during this reaction suggests that the degraded polymer has resulted, for the most part, from removal of chlorine in combination with hydrogen from an adjacent carbon yielding the following structure:



Investigative work reported by the National Lead Company Research Laboratories has confirmed the presence of polyene structures of the type indicated above. The characteristic light absorption patterns of heat degraded polyvinyl chloride were obtained and showed multiple absorption peaks in the region above 3000 Å. Such absorption curves are indicative of visible color formation. These data further demonstrated that the intensity of absorption is definitely increased by longer heat treatment. The determination of absorption peaks at higher wavelengths after longer heat treatment showed the shift of color from the yellow portion of the visible spectrum to the cause of the driving force of the heat energy put into the polymer, and oxidation occurs as a secondary reaction attacking the unsaturation developed in the polymer. Under extreme catalytic conditions, the oxidation may become the primary degradation action with the ultimate result of actual combustion.

B. LIGHT DEGRADATION

Polyvinyl chloride plastics are subjected to considerable heat during processing and fabrication, and consequently some measure of polyene unsaturation may be present when the finished compound is exposed to light. Such polyene systems absorb light within the ultra-violet range. The energy resulting from this absorption will act to re-energize the polymer chain and promote both oxidative degradation and dehydrochlorination. Since ultra-violet light is an oxidation catalyst, the oxidative type of degradation is probably predominant during the light aging life of the vinyl compound. Further split-out of hydrogen chloride will proceed to a somewhat lesser degree producing additional polyene unsaturation and increasing the possibility of even more oxidation. In addition, hydrogen chloride itself definitely catalyzes oxidative attack on the double bonds under exposure to ultra-violet light.* Primary light failure of vinyl chloride type plastics will evidence itself more through embrittlement and tackiness typical of oxidation, with increased color formation as a secondary failure.

In this manner, the difference between light and heat induced degradation may be evidenced. The dual mechanism of oxidation and hydrogen chloride loss occurs in both types of degradation. The essential differences are in degree rather than type of degradation. As a result, the compound heat-stabilized against both dehydrochlorination and oxidation, will also be resistant to light and vice versa. In practice, however, good heat and light stability may not always be in parallel evidence. This deviation from theory is generally due to the interference of side reactions set up between stabilizer and plasticizer, colorant or filler. These reactions are under study and specific recommendations for various cases are made elsewhere in this manual. For this reason, there *cannot be a universal stabilizer,* no matter how well any one material may meet all the theoretical requirements for the ultimate in stabilization.

C. REQUIREMENTS OF AN IDEAL STABILIZER

From a consideration of the basic chemical reactions involved in heat and light degradation of polyvinyl chloride type resins, it is possible to postulate the requirements of an "ideal stabilizer" material, or combination of materials.

(1) Since the hydrogen chloride released in the dehydrochlorination reaction has given evidence of promoting the auto-catalytic nature of the ultimate degradation, it is necessary to remove or chemically combine this material as effectively as possible. Where electrical properties are required, it is essential that this chemical combination not result in an electrolytic conductor, and it is necessary to combine the hydrogen chloride into an insoluble and non-ionizable end product. Of all the metals known, only silver, mercurous mercury, and lead form insoluble chlorides. As a result, some form of reactive lead compound is the most suitable practical source of *"hydrogen chloride acceptor."* While lead compounds are the most suitable hydrogen chloride acceptors from the standpoint of chloride insolubility, there are some instances where lead compounds are not indicated, and other metal compounds, as for example, those of barium, cadmium, tin and sodium are more desirable. There are still other applications where combinations of the above materials

**Ibid*, p. 6.

III. APPLICATION OF "DUTCH BOY" LEAD STABILIZERS

A. STABILIZER REACTIVITY

The group of "DUTCH BOY" lead stabilizers described in this section have each been found to have specific chemical and physical properties that make them useful, either alone or in combination, for one or more of the varied vinyl plastic applications. Since all of these materials are lead salts, they meet the basic requirement of being an "acid acceptor," and therefore contribute to the ultimate heat and light stability in vinyl compounds. Actually, litharge (PbO) would be the most efficient form of using lead as an "acid acceptor," but the nature of vinyl stabilization goes beyond mere acid acceptance, and various other chemical and physical actions must be incorporated into a desirable stabilizer compound or combination. It must be noted that litharge is not light and color stable and may be used only in certain black pigmented compounds.

Basic lead carbonate has long been an important paint pigment. Chemically, basic lead carbonate may be represented as $2PbCO_3 \cdot Pb(OH)_2$. The total PbO content is 85% but only 28-31% is in the available basic portion of the molecule. Reaction of PbO beyond this available 28-31% will evolve CO_2 and give the phenomenon of "gassing."* From this, it may be seen that in a lead stabilizer there are two considerations, reactive and safe PbO content, which are, of course, both related to the total PbO content. In the case of basic lead carbonate there is 85% total and reactive PbO, but only 28-31% safe PbO. These considerations should be kept in mind in choosing the proper stabilizer for a vinyl compound. In many cases, the total reactive basicity must be limited because of the chemical nature of the plasticizer, colorants, and fillers used. A study of the chemical compositions of "DUTCH BOY" lead stabilizers will indicate the total, reactive, and safe PbO in each of these materials.

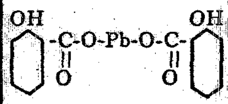
Electrical properties are of prime importance for the many kinds of insulation and dielectric materials in which vinyl chloride resins are used. Such application is a prime example of a situation where the lead stabilizer is most necessary. The stabilization mechanism proceeds by reaction with the hydrogen chloride released during processing and aging, and must result in an insoluble, non-ionizable material. Lead is the only economical material which forms an insoluble, non-ionizable chloride. For this purpose "DUTCH BOY" TRIBASE, DYTHAL, DYPHOS, LECTRO "60", TRIBASE-E and DS-207 have been found exceptionally desirable.

B. PLASTICIZER-STABILIZER INTERACTION

A stabilizer may very satisfactorily impart good heat and light resistivity into the polymer, but in so doing, may react with the plasticizer and give rise to loss of plasticity or severe color formation or both. At the temperatures of processing used for the average vinyl application, plasticizer-stabilizer-resin interaction is almost inevitable. It is, therefore, necessary to form reaction products which are non-colored and possess desirable stabilizing effects. In some cases, it is desirable to keep stabilizer-plasticizer interaction to as low a degree as possible. Some stabilizers may be added for the purpose of directing or modifying this plasticizer- stabilizer interaction (actually stabilize the plasticizer).

*Gassing may be defined as the rapid evolution from the plastic compound of a gaseous or easily vaporized substance. This action results in an uneven pock-marked surface and/or porous interior. Gassing is generally caused by decarbonation reaction with fillers, stabilizers, pigments, etc., vaporization of occluded moisture, rapid split-out of hydrogen chloride, or presence of volatile plasticizers and solvents, etc.

"DUTCH BOY" LEAD STABILIZERS

LECTRO "60"	NORMASAL	PLUMB-O-SIL B	PLUMB-O-SIL C	TRIBASE	TRIBASE E
Lead Chloro-silicate Complex	Normal Lead Salicylate	Coprecipitated Lead Orthosilicate and Silica Gel	Coprecipitated Lead Orthosilicate and Silica Gel	Monohydrous Tribasic Lead Sulfate	Basic Lead Silicate Sulfate
Complex structure		Complex structure	Complex structure	$3PbO \cdot PbSO_4\ H_2O$	Complex structure
—	481	—	—	991	—
47.5 36.1 36.1	46.5 — 46.5	51 25-51 25-51	47 23-47 23-47	89 67.3 67.3	68 50.8 50.8
fine white powder	soft creamy white crystalline powder	soft white powder	soft white powder	fine white powder	fine white powder
47% SiO_2 3% Cl	57.4% salicylic acid	42.6% CiO_2	38.3% SiO_2	8.1% SO_3	23.9% SiO_2 6.1% SO_3
2.1	1.78	1.58-1.60	1.58	2.1	2.1
4.0	2.36	3.3	2.96	7.1	5.55
insoluble in all common solvents	0.5% sol. in water; sol. in glycols, glycol ethers. Sl. sol. methyl and ethyl alcohol.	insoluble in all common solvents	insoluble in all common solvents	insoluble in all common solvents	insoluble in all common solvents
Economical stabilizer for vinyl electrical and calendered products	Anti-oxidant and light screening agent	Translucent polyvinyl chloride resins	Translucent polyvinyl chloride resins (Specially treated for easy dispersion)	High quality electrical vinyl compounds	Economical electrical stabilizer for vinyl chloride
Types I, IIA & B, III, IV	Type II (Special for asbestos filled flooring stocks, see page 34)	Types I, IIA & B, III, IV	Types I, IIA & B, III, IV	Types I, IIIA, IV, IIA for electrical insulation	Types I, IIIA, IV, IIA for electrical insulation
II, III, XXIII	XIV, XV		IX, XX, XXI, XXIII, XXVI, XXVII, XXIX	I, V, XV, XXXI, XXXV, XXXIX	I, II

around stabilizer. Outdoor weathering tests show conclusively that DYPHOS is superior to all other stabilizers with this group of plasticizers.*

Phosphate Type

In Type II plasticizers, the nature of the organic portion governs the choice of stabilizer. Where the aryl group is cresyl, the reactive basic lead stabilizers will probably cause formation of free cresylic acid and result in discoloration under exposure to either heat or light. This acid formation with resultant poor stability seems to apply in the general case of aryl phosphates. The use of "DUTCH BOY" PLUMB-O-SIL B or C, or "DUTCH BOY" LECTRO "60" has been found desirable for stabilization of formulations with aryl phosphate and mixed aryl-alkyl phosphate (Types II A and II B) plasticizers. This is an excellent illustration of the effectiveness of the PLUMB-O-SILs and LECTRO "60" in providing the desirable properties of lead stabilizers with a minimum of the apparent reactivity of basic lead. In some instances, NORMASAL appears to inhibit formation of cresylic acid and related products. In special cases, where the Type II A plasticizers (aryl phosphates) are used in electrical insulation compounds, TRIBASE, LECTRO "60", TRIBASE-E, DYPHOS, or DYTHAL are recommended. These basic lead stabilizers should be used with such plasticizers when excellent electrical properties in a stabilizer are the primary requirements. DYPHOS imparts the best heat and light stability to vinyl compounds containing large amounts of the alkyl phosphate (Type II C) plasticizers.

Admittedly there are several types of applications involving the use of Type II plasticizers where lead stabilization is not indicated. Numerous examples of such non-lead stabilization with Type II plasticizers will be found in the section entitled "APPLICATION OF 'DUTCH BOY' NON-LEAD STABILIZERS" beginning on page 17.

Oil Type

With the Type III A plasticizers (organic ester epoxides), the basic lead stabilizers, DYPHOS, DYTHAL, TRIBASE, TRIBASE-E, and LECTRO "60" provide very good heat and light stability. It should be noted that "DUTCH BOY" LEADSTAR, normal lead stearate, is recommended rather than DS-207 when lubrication is desired in compounds containing these plasticizers.

In the case of oxidizable Types III B and III C plasticizers, basic lead appears to have a detrimental effect which is generally evidenced by poor heat aging properties. This is particularly apparent through the discoloration and occasionally more pronounced "spewing"** of the vinyl compositions. LECTRO "60" is a notable exception to this rule. The shielded reactivity of LECTRO "60" and "DUTCH BOY" PLUMB-O-SIL B and C has been found particularly outstanding in both heat and light aging with plasticizers of this general type. In addition, any tendency towards spewing is inhibited, probably by adsorption on the activated silica gel of PLUMB-O-SIL. As a result, LECTRO "60" and PLUMB-O-SIL B and C provide the best stability for compounds in which Type III B or C plasticizers predominate, and also act as anti-blocking agents to reduce any tendency toward spewing.

Though Types III B and C plasticizers are difficult at best to stabilize with any type of stabilizer, it is sometimes necessary by reason of cost or other considerations to

*Hendricks and White, *Ind. Eng. Chem.*, **43**, 2335 (1951).

**Spewing may be defined as migration to the surface of some component of the vinyl plastic compound which (1) is initially incompatible, (2) is compatible at processing temperatures but less compatible at room temperature, (3) becomes incompatible due to compound breakdown.

Mixtures of Plasticizer Types

In commercial practice, it is the exception when only one plasticizer, or even one type of plasticizer is used in the vinyl compound. There are many reasons for using combinations of plasticizers from the various groups. Among these are economy, availability, and specific properties sought. As a result, a typical film compound may have plasticizers from Types I, II, and III or IV present. In such cases, since the total effect on stability is generally additive, combinations of specific stabilizers for each general plasticizer grouping may be successfully and advantageously used. In some cases, when the total plasticizer used consists primarily of the types where a highly basic stabilizer is detrimental, it may be desirable to stabilize as though the entire plasticizer system were of this order of reactivity. For these cases, "DUTCH BOY" non-lead stabilizers should be used. (See Section IV, pp. 17-25.)

D. LUBRICATION

For successful processing of a vinyl compound, it is desirable and necessary to use lubricants. Various lubricants including waxes, stearic acid, "DUTCH BOY" CALSTAR (calcium stearate), "DUTCH BOY" LEADSTAR (normal lead stearate), and "DUTCH BOY" DS-207 (dibasic lead stearate) have been used. The first four are all molten at processing temperatures and have reduced lubrication value as the temperature rises. "DUTCH BOY" DS-207 does not melt (decomposes above 600°F.) and maintains a constant solid phase lubrication over the entire heat processing history. Since DS-207 is almost entirely insoluble in most plasticizers, and does not become molten, it does not enter the plasticizer phase of the compound, and is not carried to the surface. The over-all compatibility of DS-207 is greater than any other lubricant mentioned.

Stearic acid is less compatible than either calcium stearate or lead stearate, and, in concentrations much over 0.75%, tends to spew severely to the surface. The normal soaps, CALSTAR (calcium stearate) and LEADSTAR (lead stearate), react with the hydrogen chloride released from the polymer and give some degree of stability. This reaction, of course, frees stearic acid and promotes spewing, in the absence of primary stabilization. "DUTCH BOY" DS-207, $2PbO \cdot Pb\ (C_{17}H_{35}COO)_2$, as may be seen from its structure, has two additional PbO groupings which must be reacted before any stearic acid is released into the vinyl compound. As a result, "DUTCH BOY" DS-207 is less prone to promote spewing and offers greatly enhanced heat and light stability over these other materials. This is another application of the concept of total, reactive, and safe PbO content. Use of DS-207 in the normal lubricant concentrations with the other "DUTCH BOY" lead stabilizers will double or even treble the heat and light resistance of the compound in many cases.

E. STABILIZER TINTING STRENGTH

The ultimate application of a vinyl compound may require complete translucency, a high degree of translucency, complete opacity, or any number of vivid or pastel colors. Lead stabilizers are not suitable for the obtaining of crystal clear transparency. For most so-called "clear" applications, a high degree of translucency, with opacity no greater than that contributed by a matted calender, is all that is required. Since, in effect, the "DUTCH BOY" lead stabilizers are actually pigments with stabilizing properties, it is well to differentiate between their relative "tinting strengths."*

*Tinting strength is related directly to the difference in refractive index of vehicle and pigments. The greater this difference the greater is the scattering of light and the more apparent becomes the opacity or pigmenting effects. Titanium dioxide pigment has a refractive index of about 2.5, while vinyl resins have refractive indices of 1.58 to 1.67. The difference of approximately 1.0 gives the maximum tinting strength which is obtainable with the pigments in common usage today. A pigment with a refractive index equal to or similar to that of the resinous vehicle would have little apparent opacity or tinting strength.

IV. APPLICATION OF "DUTCH BOY" NON-LEAD STABILIZERS

"DUTCH BOY" lead stabilizers provide the best heat and light stability available for the vast majority of vinyl plastic applications. The long experience of the vinyl industry with "DUTCH BOY" lead stabilizers has established their efficiency, versatility and economy. In general, it is necessary to utilize vinyl stabilizers, other than lead, for certain end-use requirements, or in conjunction with certain special compounding ingredients. For cases where lead stabilizers cannot be used, or are not desirable, the National Lead Company, through its Research Laboratories, has developed a new line of non-lead stabilizers. Proper application of appropriate "DUTCH BOY" vinyl stabilizers, both lead and non-lead, enables the vinyl plastics compounder to stabilize effectively almost any type of vinyl end-product he is called upon to produce.

A. CONSIDERATIONS IN CHOOSING NON-LEAD STABILIZERS

There are four separate reasons why application of the "DUTCH BOY" non-lead stabilizers may be necessary or desirable.

1. Clarity

There are some plastic end-products requiring a high degree of transparency, greater than that available through use of the highly translucent lead stabilizers, such as PLUMB-O-SIL B or C, DS-207, LEADSTAR, etc. Notable examples of such products are transparent calendered film and sheeting, extruded clear garden hose, certain types of belting, clear phonograph records, plastisols, organosols and solution coatings. "DUTCH BOY" non-lead stabilizers may be used to advantage in clear products in all these classifications.

2. Staining

Some vinyl plastic products are used in atmospheres containing hydrogen sulfide or other sulfides where the possibility exists of reaction with the stabilizers used. Lead sulfide formation, leading to highly colored reaction products, is often observed when lead stabilizers are used. The result is the formation of brown, black, or yellow staining of the stocks. Another frequent source of sulfide staining is the use of sulfite process wrapping paper and cardboard containers. In cases where a high degree of staining resistance is required, use of "DUTCH BOY" non-lead stabilizers is recommended. Vinyl sheeting used as upholstery, vinyl light gauge sheeting used for curtains, draperies and table cloths, and stain resistant vinyl flooring are a few of the end-products where "DUTCH BOY" non-lead stabilizers may be used to advantage.

It should be emphasized, however, that stain resistance is only one of a great many desirable properties which must be built into quality vinyl products. Very often, some very important advantages may be compromised in formulation of a completely stain-resistant stock, and it is up to the good judgment of individual compounders to decide which are the most important properties for a particular end-use.

3. Toxicity

Only a very small percentage of vinyl plastic products are required to be completely non-toxic. Included in this group are food packaging film, and surgical and beverage tubing. There are a great many other products which, while not required to be non-toxic, are still sometimes formulated by manufacturers without use of lead stabilizers, as a safety measure. Examples of this type are vinyl baby clothing and accessories, and slush molded toys. In most cases, complete non-toxicity in products is neither necessary nor possible, simply because the physical properties required are attainable only through use of plasticizers which are not, in themselves, non-toxic in nature. Excellent stabilization may be achieved through the use of "DUTCH BOY" non-lead stabilizers, even slightly less lubricating action than CLARITE. It develops lower viscosity in plastisols than CLARITE, and is particularly recommended for use with easily oxidized plasticizers.

PROVINITE has the best electrical properties of the barium-cadmium type stabilizers. Although its electrical properties are not equal to the standard lead stabilizers, PROVINITE is highly satisfactory for clear and brightly colored jacketing stocks for instrument wires, novelty Christmas tree wire, and other low requirement wire coatings.

PROVINITE's combination of stabilizing properties is especially suitable for calendered vinyl stocks, where resistance to oxidation and sharp retention of color are essential. It may be used at concentrations ranging from 2% of PROVINITE A and 1% of PROVINITE B in high temperature sheeting stocks to as low as 0.75% of the A and 1% of B in thin film. The use of the lower concentrations provides even better clarity and less lubrication than the conventional level of usage. An excellent non-staining film stock may be achieved through the use of a small quantity of "DUTCH BOY" NALZIN with PROVINITE, as described below.

Barium-cadmium organic stabilizers are well established for clear and highly translucent compositions. One serious limitation of these systems is their tendency to stain in contact with sulfur or sulfur-containing materials. It has long been known that small amounts of organic zinc compounds eliminate or minimize the staining tendency of barium-cadmium stabilizers. Presumably this is due to the preferential acceptance of the sulfur compounds by the organic zinc salt to form a soluble or light colored sulfide.

"DUTCH BOY" NALZIN is a zinc organic complex especially developed for co-use with barium-cadmium stabilizers to eliminate sulfur staining. NALZIN should always be used in accordance with recommendations, since in large amounts, zinc compounds can readily become degradation catalysts instead of stabilizers for vinyls.

The exact level of NALZIN needed in a particular formulation depends to a large extent on the level of the barium-cadmium stabilizer, the sulfur staining resistance requirements, and the processing conditions. The optimum ratio, based on barium-cadmium content, is approximately 15% NALZIN, based on FLOMAX 25, or 25% NALZIN, based on PROVINITE A. For example, 3% FLOMAX 25 (based on the resin) should be changed to 2½% FLOMAX 25 with 0.5% NALZIN, where freedom from sulfide staining and optimum heat stability are required. Correspondingly, 2% PROVINITE A and 1% PROVINITE B should be changed to 1.5% PROVINITE A, 0.5% NALZIN, and 1% PROVINITE B (all on resin basis). *Under no circumstances should NALZIN be used alone without supplementary stabilization.*

"DUTCH BOY" FLOMAX 25 is a liquid barium-cadmium organic stabilizer. It is readily incorporated and imparts the highest degree of clarity of all of the "DUTCH BOY" stabilizers. FLOMAX 25 is entirely compatible with vinyls and it shows very little plating tendency. FLOMAX 25 gives vinyl film an ideal surface for heat sealing and printing, since it provides a dry and tack-free surface. It is recommended for plastisols, organosols and solution coatings because of its ready dispersibility, low viscosity, clarity and compatibility. The heat stability of FLOMAX 25 is almost on a par with the CLARITE-PROVINITE class of stabilizers for extended heat exposure at very high temperatures. It is excellent for the normal processing conditions used in calendering, extrusion and dispersion resin fusions. The light stability is remarkably good, being equal to or better than that of PROVINITE. For most vinyl stocks, FLOMAX 25 is recommended at a level of approximately 3% on the resin, subject to requirements for special heat conditions. Vinyl film is generally successfully stabilized with 2.5% FLOMAX 25 together with about 0.5% stearic acid. From 2% to 3% FLOMAX 25 is best for dispersion and solution vinyl resin systems.

"DUTCH BOY" NON-LEAD STABILIZERS

FLOMAX 25	NALZIN	PROVINITE PROVINITE A	PROVINITE PROVINITE B
Barium-Cadmium Organic Complex	Zinc Organic Complex	Barium-Cadmium Organic Complex	
Complex Structure	Complex Structure	Complex Structure	
—	—	—	—
Clear yellow liquid	Clear pale yellow liquid	soft white powder	clear straw-colored liquid
1.48	1.46	1.56 max.	1.51
1.03	0.916	1.31	0.995
miscible in mixtures of hydrocarbon solvents with ketones, esters, "Cellosolves," etc.	miscible in mixtures of hydrocarbon solvents with ketones, esters, "Cellosolves," etc.	insoluble in all common solvents	miscible in mixtures of hydrocarbon solvents with ketones, esters, "Cellosolves," etc.
		Supplied as a two part system General Recommendation: 0.75 to 2 parts PROVINITE A 1 part PROVINITE B per 100 parts of resin	
Liquid stabilizer with very high clarity and excellent plating resistance.	Supplementary stabilizer for barium-cadmium types to resist sulfide stain.	General purpose clear heat and light stabilizer, for calendering, extrusion and dispersion resin applications.	
Types I, II, III, IV, VIA; VIB with NALZIN	Types I, II, III, IV, VI	Types I, II, III, IV, VIA; VIB with NALZIN	
VII, XVII, XVIII, XIX, XXI, XXV, XXVII, XXXVII, XL	X, XVIII, XXV, XL	VI, X, XXIV, XXVI, XXXVI	

CLASSIFICATION OF VINYL PLASTICIZERS

TYPE I *Organic Ester Type* (Phthalates, adipates, azelates, sebacates, which do not contain ether linkages or aliphatic unsaturation)

- A. Primary* type plasticizer
- B. Primary type plasticizer of highest quality with special properties such as low temperature flexibility or low volatility, etc.

TYPE II *Phosphate Type*

- A. Aryl phosphates
- B. Aryl-alkyl phosphates
- C. Alkyl phosphates

TYPE III *Oil Type***

- A. Organic ester epoxides
- B. Ether esters (Polyethylene glycol esters, etc.)
- C. Aliphatic unsaturated esters (Unsaturated oil derivatives)

TYPE IV *Polyester Type* (Polymerics, semi-polymerics)

TYPE V *Chlorinated Type* (Chlorinated paraffins and aromatics)

TYPE VI *Miscellaneous Type*

- A. Hydrocarbons, nitriles, amides, etc.
- B. Sulfur containing materials

D. RECOMMENDED NON-LEAD STABILIZATION FOR VARIOUS PLASTICIZER TYPES

Organic Ester Type

Plasticizers of Type I present relatively few problems in stabilizer choice. Excellent performance is obtained by the use of the barium-cadmium organic stabilizers such as CLARITE, PROVINITE, and FLOMAX 25. The choice among these stabilizers is governed chiefly by the type of products being manufactured and their stability and clarity requirements. For example, for maximum heat stability PROVINITE or CLARITE is suggested; for maximum light stability PROVINITE or FLOMAX 25 would be selected; for maximum clarity FLOMAX 25 is recommended. The specific advantages and recommendations for these stabilizers were outlined earlier in this section.

Where outstanding weathering resistance is desired in films, organosol coatings and vinyl solution coatings containing Type I plasticizers, "DUTCH BOY" CS-137 should be used in conjunction with PROVINITE or FLOMAX 25.

Phosphate Type

As mentioned previously, the Type II plasticizers often present a problem in satisfactory stabilization. "DUTCH BOY" PROVINITE, CLARITE, and FLOMAX 25 are exceptionally effective in promoting high heat and light stability in Type II plasticizers, with PROVINITE the best of this group by a small margin. Whenever any of the barium-cadmium stabilizers are employed with phosphate plasticizers, a small amount of epoxidized plasticizer (Type III A) adds to heat stability.

*A primary plasticizer may be classified as a plasticizer which *of itself* will produce the required degree of flexibility in a vinyl plastic without the serious defects of inefficiency, instability or incompatibility. The use of only a primary plasticizer will give good general properties to the vinyl compound. It is often desirable to modify the primary plasticizer composition with *secondary plasticizers* which would have the virtue of lower cost or some special chemical or physical property.

**This classification is based on the consideration that both the aliphatic carbon to carbon unsaturated bond and the ether linkage are readily oxidized. Plasticizers containing these groupings are subject to cleavage and may loose their original compatibility in the vinyl compound, and as a result may spew.

a combination of CS-137 and FLOMAX 25 is suggested. The anti-oxidizing action of CS-137 and the excellent light stability of this stabilizer combination will greatly help to "stabilize" both the vinyl resin and Type VI A plasticizers.

A combination of "DUTCH BOY" NALZIN and FLOMAX 25 is especially recommended for stabilizing vinyl compounds containing Type VI B plasticizers (sulfur-containing materials). In addition to its very good all-around stabilizing action, this combination does not cause undesirable sulfide staining in the presence of these plasticizers. CS-137 is also resistant to sulfide staining, as well as being an excellent light stabilizer. It is recommended as a secondary stabilizer with PROVINITE or FLOMAX 25 in those vinyl compounds which must have extreme resistance to outdoor weathering and ultra-violet light. When added lubrication is desired for easier processing or better mold release in compounds containing the Type VI B plasticizers, CALSTAR is very efficient.

Mixtures of Plasticizer Types

It should be remembered that the usual practice in vinyl compounding is to use several plasticizers, often of several types or groups, to get the specific properties desired in various products. The contribution of each plasticizer as far as stabilization techniques are concerned is generally additive. Thus, the stabilizer system used for a mixture of plasticizers will be made up of proportional amounts of the stabilizer that would be used if each plasticizer were considered alone. Very often, where a formulation contains a large amount of a plasticizer other than Type I, which tends to be reactive or difficult to stabilize, it is necessary to select a stabilizer system as if the entire plasticizer content were of this order of reactivity. In this respect, use of "DUTCH BOY" non-lead stabilizers is similar to lead stabilization. The section on "Practical Compounding" gives many helpful stabilizer suggestions for specific cases.

E. LUBRICATING PROPERTIES

Two of the "DUTCH BOY" barium-cadmium stabilizers, CLARITE and PROVINITE, possess sufficient lubricating properties of themselves, so that supplementary lubrication is not normally required for most applications. FLOMAX 25 has no lubricity. Among the non-lead stabilizers, "DUTCH BOY" CALSTAR is the best overall lubricant. The lubricating properties of CALSTAR are superior to those of the barium-cadmium compounds. On the other hand, the heat stability protection afforded by CALSTAR is definitely inferior to that of the other "DUTCH BOY" non-lead stabilizers.

F. OTHER CONSIDERATIONS

"DUTCH BOY" non-lead stabilizers are not suitable for primary insulation. The unique requirement of high volume resistivity makes complete absence of soluble or ionizable compounds in electrical formulations desirable. Lead stabilizers are considered mandatory for this application. For secondary insulation or jacketing stocks, however, "DUTCH BOY" PROVINITE can be used when special effects are required, such as in clear, highly colored insulation novelties.

Additional methods have been utilized to obtain shorter pre-mixing and fluxing cycles. They shorten the time in which the plastics compound will be subjected to high temperatures and insure more complete wetting of stabilizer and resin by the plasticizer. Notable among these is the use of stabilizers specially treated for ease of dispersion. "DUTCH BOY" PLUMB-O-SIL C, TRIBASE-E and LECTRO "60" are outstanding materials of this type, and they wet and disperse very easily in plastic mixes. They will be found very useful in all applications where stabilizer dispersion is a problem.

The technique of masterbatching has been very successfully employed in obtaining the degree of dispersion necessary for better ultimate stability. Not only does masterbatching insure this necessary dispersion, but it also allows easier handling and results in a more uniform product. The dispersion of stabilizer in plasticizer to form a stabilizer paste is a very obvious method of masterbatching. In this method, the stabilizer is dispersed in plasticizer by grinding on a three-roll paint mill, in a colloid mill, or in a ball mill. The dispersion of stabilizer in resin has also been successfully employed and may be utilized in masterbatch chip form, or may be made into a solvated semi-paste.

Other methods of processing vinyls, such as coating, dipping and casting, which utilize organosols, plastisols and emulsion dispersions, have also successfully utilized pre-dispersed stabilizers. Actually, masterbatches may cut the required grinding time needed for the total organosol or plastisol.

stripfeed the extruder. Temperatures of 300° to 350° F. for periods of ten to thirty minutes are encountered during such operations. Hot-stripfeed stock may stay on the warm-up mill for a longer period, but is compensated by a shorter cycle in the extruder.

The entire fluxing and mixing may be carried out directly on a large two-roll hot plastics mill. Cycles up to forty minutes at temperatures of 300° to 360° F. are encountered under such conditions. Temperatures in the extruder for hot mixed compounds may range up to 375° F., but generally for shorter periods than required for dry mixed compounds.

Electrical Compounds

Two broad classes of compounds are employed in the electrical field, primary insulation for wire coating, and jacketing or secondary insulation for the mechanical protection of primary insulated wires. Primary insulation, applied directly over the conductor to provide electrical protection for the system, must necessarily have a high insulation resistance, and the maintenance of flexibility and electrical properties during long-term exposure to heat and moisture is of paramount importance. Selected clay fillers are incorporated to increase insulation resistance, but amounts higher than ten to fifteen percent by weight are usually avoided so as not to impair physical properties and lower the heat stability. A high resistance to deformation is desirable in preventing the wire from cutting through the insulation during handling and installation.

In primary insulation "DUTCH BOY" TRIBASE, TRIBASE-E, LECTRO "60" and DYTHAL have been found exceptionally desirable, since their heat stabilizing action and electrical properties are outstanding, and unusual light stability is not generally required.

"DUTCH BOY" TRIBASE ($3PbO{\cdot}PbSO_4{\cdot}H_2O$) has a total PbO content of 89%, of which 67% is reactive and safe. This high basic lead content affords excellent electrical characteristics with most of the commonly used electrical plasticizers without any danger of color instability, gassing, or moisture pick-up. TRIBASE is the quality electrical stabilizer for primary insulation.

"DUTCH BOY" TRIBASE-E is a specially prepared basic lead silicate sulfate containing 68% total PbO, of which 50.8% is safe and reactive PbO. It gives excellent electrical properties of the same order of magnitude as TRIBASE, but it does not possess the reserve heat stability of TRIBASE, although it is superior to basic lead carbonate and other similar pigment materials. The low specific gravity of TRIBASE-E (5.5) makes this material an economical, general stabilizer for primary insulation compounds.

"DUTCH BOY" LECTRO "60" is a lead chlorosilicate complex which possesses excellent electrical properties and good heat stability combined with ready dispersability. LECTRO "60" has outstanding moisture resistance and retention of electrical properties on long-term water immersion. It is particularly recommended for applications, such as TW wire where good long term water immersion characteristics are essential. LECTRO "60" can be used with a wide range of plasticizers including certain polymerics, phosphates and unsaturated or ether esters. In addition, its low specific gravity (4.0) makes LECTRO "60" the most economical "DUTCH BOY" stabilizer for primary insulation.

"DUTCH BOY" DYTHAL, with a total PbO content of 79.8% of which 54.6% is safe reactive PbO, compares favorably with TRIBASE in stabilizing vinyl insulation, and is particularly useful in high-temperature appliance wire formulations. In fact,

FORMULA II

Low-Cost General Purpose Insulation

Resin	100
Type I A Plasticizer	27
Type I A Plasticizer (low cost)	15
Type III A Plasticizer	8
Type V Plasticizer	5
Type VI A Plasticizer	5
Filler	25
TRIBASE-E or LECTRO "60"	7
LEADSTAR	1

FORMULA III

TW Type Insulation (60° C.)

Resin	100
Type I A Plasticizer	40
Type IV Plasticizer	7-12
Filler	10-15
LECTRO "60"	7
DS-207	0-1

FORMULA IV

High Temperature Appliance Type Insulation (105° C.)

Resin	100
Type I B Plasticizer	15
Type IV Plasticizer	45
Filler	10-20
DYTHAL	7
DS-207	0-1

FORMULA V

Low Temperature Jacketing

Resin	100
Type I A Plasticizer	40
Type I B Plasticizer	20
Filler	0-10
TRIBASE or DYPHOS*	6
DS-207	0-1

*Especially recommended for outdoor exposure.

FORMULA VII

Clear Garden Hose

Resin	100
Type I A Plasticizer	25
Type I A Plasticizer (low cost)	15
Type III A Plasticizer	5
Type III B Plasticizer	10
FLOMAX 25	2.5
Stearic Acid	0.5

FORMULA VIII

Opaque Garden Hose

Resin	100
Type I A Plasticizer	25
Type I A Plasticizer (low cost)	15
Type III B Plasticizer	20
Filler	20-40
DYPHOS	4
DS-207	0.5-1

FORMULA IX

Translucent or Brightly Colored Belting (Flame Resistant)

Resin	100
Type I A Plasticizer	25
Type II B Plasticizer	15
Type III B Plasticizer	15
PLUMB-O-SIL C	4
DS-207	0.5-1

FORMULA X

Clear Non-Staining Welting

Resin	100
Type I A Plasticizer	20
Type I B Plasticizer	10
Type II B Plasticizer	15
Type III A Plasticizer	5
PROVINITE A	1
PROVINITE B	1
NALZIN	0.25

"DUTCH BOY" CLARITE A is highly recommended in conjunction with NORMASAL for standard asbestos-filled stocks. Application of this principle is illustrated in FORMULA XIV. CLARITE provides the additional heat stability necessary for these systems, particularly when Type II plasticizers are used in the formulation.

In heavy duty applications, where more stringent requirements for heat stability exist, the more basic stabilizers such as TRIBASE, DYTHAL, DYPHOS, TRIBASE-E, and LECTRO "60" are used, the selection depending on the heat and light stability desired, as has been discussed previously. FORMULA XV illustrates the use of NORMASAL and TRIBASE for primary heat stability of an asbestos-filled stock.

FORMULA XIII

Standard Semi-Rigid (Non-Asbestos)

Resin	100
Type I A Plasticizer	35
Type III A Plasticizer	5
Filler	200
CLARITE A	2
CALSTAR	1

FORMULA XIV

Standard Asbestos Semi-Rigid

Resin	100
Type I A Plasticizer	60
Type III A Plasticizer	10
Asbestos Filler	140
Filler	130
TITANOX RA-50	25
NORMASAL	7
CLARITE A	2
CALSTAR	1

FORMULA XV

Heavy Duty Asbestos Semi-Rigid

Resin (special low molecular weight vinyl copolymer)	100
Type I A Plasticizer	20
Type I B Plasticizer	5
Type V Plasticizer	10
Asbestos Filler	100
Filler	250
TITANOX RA-50	10
NORMASAL	6
TRIBASE	2
LEADSTAR	1

requirements. Proper stabilization follows the general principles which have been previously outlined, using the more basic stabilizers where maximum heat stability for processing and reworking is needed.

For outstanding clarity and resistance to yellowing and plate out, "DUTCH BOY" FLOMAX 25 is the first choice for film or sheeting. The heat and light stability contributed by FLOMAX 25 is of a high order. FLOMAX 25 can be successfully used with a wide range of plasticizers, including the more sensitive types, and consequently enables the compounder to formulate with the widest possible latitude. Since FLOMAX 25 is entirely liquid, it is also the easiest of all the "DUTCH BOY" stabilizers to disperse. FLOMAX 25 has no lubricating properties. A small amount of stearic acid is often a valuable aid in processing.

"DUTCH BOY" PROVINITE is recommended for the heavier type of sheeting and other high quality applications, where a clear stabilizer is required with an excellent combination of heat and light stability. The heat stability of PROVINITE is slightly above that of FLOMAX 25, while PROVINITE's light stabilizing action is nearly equal to FLOMAX 25. PROVINITE combines high clarity with good resistance to yellowing. Of itself, PROVINITE has a definite lubricating action in vinyl plastic stocks. When formulations are based on PROVINITE, the individual case will determine whether any additional lubricants will be required.

Where complete freedom from sulfide staining is mandatory, "DUTCH BOY" NALZIN may be combined with either FLOMAX 25 or PROVINITE. Recommended amounts of NALZIN are discussed in detail on page 19, and several examples of non-staining stocks are shown in the formulations below.

"DUTCH BOY" PLUMB-O-SIL's are among the most versatile and popular stabilizers in the entire field of calendered vinyl products. If sensitive and reactive plasticizers and colorants are present, the ability of both PLUMB-O-SIL B and PLUMB-O-SIL C to provide excellent stability with a minimum of reactivity is extremely helpful. The additional properties of PLUMB-O-SIL B or C, such as low tinting strength, plasticizer spew absorption, and low volume cost, make them especially attractive for both translucent and opaque film. They are widely used and recommended in most types of sheeting such as whites, blacks, pastels, and vivid colors, where the same properties are desired.

For opaque film, and white pastel sheeting, the "DUTCH BOY" basic lead stabilizers are outstanding. DYTHAL and DYPHOS are used for products requiring greater reserve heat stability combined with excellent light stability. They are especially suited for heavier sheeting, where strong stabilization is needed for high-temperature calendering and reworking cycles. TRIBASE and LECTRO "60" will also provide strong heat stability. LECTRO "60" and the PLUMB-O-SILs are particularly recommended for economy in opaque film and sheeting applications.

Careful control of calendering conditions is greatly improved through the heat stabilizing action and uniform non-melting character of "DUTCH BOY" DS-207. The lubricating action of DS-207 in opaque and translucent stocks is employed to advantage in conjunction with any of the "DUTCH BOY" stabilizers. When appreciable quantities of organic ester epoxide plasticizers are present, the use of "DUTCH BOY" LEADSTAR is preferred as the lubricant.

TRANSLUCENT FILM

Useful for standard frosted finish or vivid blacks and colors.

FORMULA XX

High Quality Translucent (Flame Resistant)

Resin	100
Type I A Plasticizer	20
Type I B Plasticizer	15
Type II B Plasticizer	10
Type IV Plasticizer	5
PLUMB-O-SIL C	2-3
DS-207	0.25-1
Supplementary Stabilizer	0.5-1

FORMULA XXI

Low Cost Translucent

Resin	100
Type I A Plasticizer	18
Type I A Plasticizer (low cost)	17
Type II A Plasticizer	10
Type III A Plasticizer	5
PLUMB-O-SIL C	3
FLOMAX 25	1

OPAQUE FILM

These stocks may be made flame resistant either by including 8 to 10 parts of Type II or Type V plasticizer, or by the use of 3-5% antimony oxide, based on the resin.

FORMULA XXII

High Quality Opaque*

Resin	100
Type I A Plasticizer	25
Type I B Plasticizer	15
Type IV Plasticizer	10
DYPHOS	5
DS-207	0.5-1

FORMULA XXIII

Low Cost Opaque

Resin	100
Type I A Plasticizer	15
Type I A Plasticier (low cost)	20
Type II A Plasticizer	10
Type III C Plasticizer	10
Filler	10-20
PLUMB-O-SIL C	3
LECTRO "60"	2
DS-207	1

*This stock is especially recommended for outdoor weathering applications.

FORMULA XXVIII

High Quality Base for Whites and Pastels*
(Flame Resistant)

Resin	100
Type I A Plasticizer	23
Type I B Plasticizer	15
Type II B Plasticizer	10
Type IV Plasticizer	10
DYPHOS	5
DS-207	0.5-1

FORMULA XXIX

Low Cost Base for Whites and Pastels

Resin	100
Type I A Plasticizer	10
Type I A Plasticizer (low cost)	20
Type III A Plasticizer	10
Type III C Plasticizer	15
Type V Plasticizer	5
Filler	10-40
PLUMB-O-SIL C	4
DYTHAL	2
LEADSTAR	0.5-1

E. MOLDING COMPOUNDS

Compression Molding

Molding of vinyl chloride resins has been primarily in the field of compression molded unbreakable vinyl records. These vinyl compounds are based on the lower molecular weight copolymer resins and are used with very little plasticizer, if any, to reduce "sag"** characteristics. Any tendency to such "buttery" qualities will promote poor wear resistance and reduce high fidelity. The use of "DUTCH BOY" DS-207, in vinyl records containing fillers, has been found to promote the maximum degree of fidelity of reproduction in lateral phonograph records thus far measured by independent manufacturers. When transparent rigid recordings are desired, "DUTCH BOY" CALSTAR is the logical choice for a lubricant-stabilizer.

The compounds may be mixed by several procedures. In general, it is desirable to preblend the ingredients thoroughly in a ribbon blender, tumbler, or dough mixer before any fluxing operations are carried out. Use of a Banbury mixer in a four to eight minute cycle at temperatures of 275° to 300° F. will give satisfactory mixing and fluxing of the preblend compound. The Banbury mixed stock is then directly transferred to a worm extruder (plasticator type), where the resultant extruded web is led into a two-roll calender. The additional cycle may take four to ten minutes at temperatures averaging five to ten degrees higher than in the Banbury. The stock is scored into biscuit sections by a rotary marker as it leaves the calender. After a cooling cycle, the marked web may be broken into individual biscuits. A less elaborate scheme is to carry out the entire fluxing and mixing operation on a hot two-roll plastic mill in a ten to twenty minute cycle at 270° to 310° F. The hot stock is taken from the mill in slabs and fed to the two-roll calender as before. An additional alternate procedure is to pelletize the stock from the mill, and to extrude a sufficiently wide web which may be marked or cut by hand into biscuits.

*This stock is especially recommended for outdoor weathering applications.
**Sag may be defined as the tendency of a vinyl record to bend under its own weight or small amounts of localized pressure without the ability to completely revert to its original shape, resulting in permanent deformation.

FORMULA XXXIII

Alternate Low Cost Record Formulation*

Resin (low molecular weight vinyl chloride copolymers)	30
70% Chlorinated Paraffin	15
Filler	51
Carnauba Wax or substitute	0.5
Carbon Black	1
DS-207	1.5
DYPHOS	1

Injection Molding

Injection molding of flexible parts from plasticized vinyl chloride resins has been successful in the automotive equipment field. It is one of the promising outlets for the expansion of vinyl resins. This development has been contingent upon the availability of satisfactory stabilizers. Two major techniques are currently utilized for injection molding. Small pellets of fluxed material may be prepared by granulating compounds slabbed off a hot two-roll plastic mill. The original fluxing is carried out by using a Banbury mixer or hot plastic mill in the time and heat cycles described previously. Injection molding temperatures of 300° to 360° F., over short time cycles, at pressures of fifteen to thirty thousand pounds per square inch are required.

For clear injection molding formulations, CLARITE is recommended for its high heat stability and clarity. DYTHAL or TRIBASE should be used for stabilizing opaque compounds during the vigorous heat cycle. These two stabilizers offer the greatest heat protection of the basic lead materials.

For best lubricating and mold release properties, DS-207 should be used in combination with the basic lead stabilizers. If additional lubricity is required with CLARITE or the other "DUTCH BOY" non-lead stabilizers, CALSTAR is the best lubricant for clear molded products.

An alternate injection molding procedure can be based on the injection molding of plastisols using formulations that will be discussed in the following section. The plastisols may be injection molded at the same temperatures and at lower pressures than those described above, but will require considerably longer time cycles to obtain thorough fluxing and full development of physical properties.

FORMULA XXXIV

Clear Injection Molding Formulation**

Resin	100
Type I A Plasticizer	25
Type II B Plasticizer	15
Type III A Plasticizer	8
Type IV Plasticizer	12
CLARITE A	3
CLARITE B	1.5
CALSTAR	1

*Records based on this type formulation are satisfactory for the 10 inch records of popular and semi-classical music. They possess good fidelity, low noise level and fair unbreakability characteristics.

**A non-sulfide staining clear injection molding compound may be obtained by adding 0.7 part of NALZIN to the above formula.

"DUTCH BOY" PROVINITE is highly recommended for clear plastisols. It is especially useful for its performance under high processing and service temperatures, with excellent retention of clarity. PROVINITE contributes excellent light stability, and maintains the color and clarity of the stock under outdoor weathering conditions. In all dispersion resin applications, the usual level is 1% each of PROVINITE A and B, based on the resin. For special high heat conditions, the amount of PROVINITE A can be increased to meet compounding requirements.

"DUTCH BOY" FLOMAX 25 is a clear liquid stabilizer which combines a number of desirable properties in dispersion resin systems. Its heat and light stabilities compare very favorably with those of PROVINITE. It is especially recommended for the highest degree of clarity. FLOMAX 25 disperses readily and develops minimum increase in plastisol viscosity on aging. It has no lubricating action, no adverse effect on adhesion, and does not plate out on mold surfaces. FLOMAX 25 is particularly useful in plastisols because its low surface tension promotes rapid and easy deaeration.

Where maximum resistance to sulfide staining is required, "DUTCH BOY" NALZIN should be used with either FLOMAX 25 or PROVINITE in accordance with the directions given on page 19.

"DUTCH BOY" CS-137 is useful in plastisols for fabric coatings where additional light stabilization is desired. It is especially suited for organosols and vinyl solution coatings, either alone or as a supplementary stabilizer. CS-137 is particularly recommended for applications in which freedom from sulfide staining is desirable.

"DUTCH BOY" DYPHOS is an outstanding stabilizer for plastisol and organosol systems. It imparts unequalled heat stability for the fusing cycles, and it is unique among all stabilizers in its ability to stabilize dispersion resins against light, to the extent that they compare favorably with the calendering and extrusion resins.

"DUTCH BOY" TRIBASE is an excellent heat stabilizer which is highly recommended for use in opaque slush molding plastisols. TRIBASE offers maximum protection during the severe heat history encountered in the molding operation.

"DUTCH BOY" DS-207 performs a special task in dispersion resin systems. It confers excellent heat stability, and its lubricating action makes it the most useful stabilizer in the field of "slush" molding, due to its two-fold performance of stabilization plus mold release.

"DUTCH BOY" PLUMB-O-SIL C is a very effective stabilizer for organosols and plastisols. It combines the advantages of low tinting strength for translucent stocks and low reactivity with plasticizers and colorants, with good heat stability and economy. PLUMB-O-SIL C has a useful ability to adsorb migratory components in highly plasticized compounds, resulting in an attractive dry surface. Due to its adsorptive ability care should be exercised when formulating with PLUMB-O-SIL C to avoid too high a viscosity in the finished system.

The control of flow properties in plastisols is readily achieved by the use of "DUTCH BOY" BENTONE 38 as a thickening agent. BENTONE 38 is of special advantage in this type of application, because its control of sag or penetration is maintained through the high temperature fusion cycle.

FORMULA XL

High Quality Clear Non-Staining Organosol

Resin (dispersion type)	100
Type I A Plasticizer	20
Type III A Plasticizer	10
Type IV Plasticizer	5
Methyl Isobutyl Ketone	33*
Xylene	43*
Naphthenic Thinner	89*
FLOMAX 25	2
CS-137	1
NALZIN	0.3

FORMULA XLI

Low Cost Organosol

Resin (dispersion type)	100
Type I A Plasticizer	25
Type I A Plasticizer (low cost)	10
Type III A Plasticizer	5
Filler	15**
Xylene	98***
Naphthenic Thinner	42***
DYPHOS	5

G. MISCELLANEOUS COMPOUNDS

The vinyl resins are so versatile in their properties and compounding possibilities that many specialized applications are being developed which cannot be treated separately here. In the coating field particularly, many special compositions and resin combinations are in everyday use. For these applications, the "DUTCH BOY" vinyl stabilizers follow the general rules of application demonstrated in the fields discussed previously.

When little or no Type II A plasticizer is used, DYTHAL and DYPHOS appear to be most satisfactory for printing inks containing the usual low molecular weight vinyl resins. The prime requisites of these inks are good light stability and adhesion. Both DYTHAL and DYPHOS contribute outstanding light resistance to vinyl printing inks. FLOMAX 25 is recommended for vinyl printing inks which must be resistant to sulfide staining.

The high heat resistance, retention of flexibility and gloss, and light stability requirements of baked vinyl resin finishes can satisfactorily be obtained by use of "DUTCH BOY" DYTHAL or "DUTCH BOY" DYPHOS. Formulation of these systems follows the suggestions made in the sections on organosols.

The successful use of "DUTCH BOY" DYPHOS in vinyl stocks containing chloroparaffins, to which we have previously referred,**** has been extended to paint systems containing chloroparaffins and chlorinated rubber. Recent work has shown that "DUTCH BOY" DYPHOS not only improves color retention and service life of such systems, but it greatly decreases the yellowing tendencies which have been characteristic of them.

We suggest the investigation of "DUTCH BOY" stabilizers for any organic products containing halogens which may be exposed to heat, light or weathering.

*This is approximately 46% solids content. Solids content down to 30 to 40% for use in very thin coatings and other similar applications may be bodied to workable viscosity by use of "DUTCH BOY" BENTONE solvent thickening agents.

**Translucent compounds containing no filler may be formulated using "DUTCH BOY" PLUMB-O-SIL B or C.

***This is approximately 53% solids content. Solids contents down to 30 to 40% for use in very thin coatings and other similar applications may be bodied to workable viscosity by use of "DUTCH BOY" BENTONE solvent thickening agents.

****See Page 14.

Note

The recommendations made in this booklet are based on our research and the research of others, and are believed to be accurate. No guarantee of their accuracy is made, however, and the products discussed are sold without warranty, express or implied, and upon condition that purchasers shall make their own tests to determine the suitability of such products for their particular purposes. Likewise, statements concerning the possible use of these products are not intended as recommendations to use these products in infringement of any patent.