Coordinated Metal Drying Catalysts.

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COORDINATED METAL DRYING CATALYSTS

by

Raymond Reever Myers

A DISSERTATION

Presented to the Graduate Faculty

of Lehigh University

in Candidacy for the Degree of

Doctor of Philosophy

Lehigh University
1952

ABSTRACT

Economical replacement of conventional drying catalysts for oleoresinous vehicles by metal complexes has been demonstrated. In addition, a means has been shown to avoid the use of the strategic metal, cobalt, in certain applications. These advantages of complex catalysts have been supplemented in many cases by unusual effects resulting from their use, such as alkali-resistance, better aging properties, and less surface hardening.

With the aid of a classification scheme for the complexing agents used in this work a correlation was obtained between the structural features of an agent and its activity. Cobalt was not upgraded significantly by any amine among the 150 tried, but was retarded by diamines, particularly the strongly basic ones. Manganese was improved by numerous amines, particularly by diamines possessing resonant structures and by certain amines of large steric requirements. Iron was susceptible to the same types of amines, and was upgraded to a greater extent in proportion to its original activity than was manganese.

The excellent correlation between structure and activity led to the development of an electronic hypothesis of catalysis in which the configuration of the d electrons of cobalt was shown on theoretical grounds to be the optimum configuration for reversible combination with oxygen. The inability of cobalt to be improved by complexing was considered a corollary of this statement; while the occurrence of complex manganese catalysts of three times the activity of cobalt was explained on the basis of the lowered energy requirements of the d orbitals of manganese, coincident with the possession by the manganese monoammine of an electronic configuration identical with cobalt.

A temporary deterrent to the use of manganese complexes in varnishes is the loss of supercatalytic ability on aging. That this obstacle can be overcome through the use of the proper complexing agent is almost certain; and that the problem can be solved economically is implied by the nature of the solutions proposed. At any rate, drier technology has been advanced to the stage at which an inexpensive drier accelerator and stabilizer can be placed on the market.

The impact of the electronic hypothesis upon present day views of complexing may be far-reaching, for it has led to the conclusion that the number of coordination positions available to an amine in aprotic solvents is fewer than the number in aqueous solutions, and has resulted in a new view of chelation in cases involving resonant structures.

A test of the hypothesis by means of cryoscopic measurements of the extent of complexing has opened new vistas in complex chemistry. The fundamental importance of this study has been demonstrated; and its bearing upon the practical aspects of drying has been pointed out.

Certificate of Approval

Approved and recommended for acceptance as a dissertation in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May 10, 1952
(Date)

A. C. Zettlemoyer
Professor in Charge

Accepted, ____________________
(Date)

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Support for this work was provided by the Harshaw Chemical Company and the Advance Solvents and Chemical Corporation. It was administered by the National Printing Ink Research Institute under the direction of Dr. A. C. Zettlemoyer, who suggested the problem.

The author is indebted to Dr. Zettlemoyer for his supervision of the research; to Dr. F. J. Fornoff for guidance to the frontiers of complex chemistry; and to Drs. E. D. Amstutz, W. W. Ewing, W. C. Walker, F. H. Healey, R. F. Muraca, R. N. Rhoda and Prof. J. G. Smull for their advice and suggestions.

Credit for much of the experimental work goes to Mr. Gilbert Epstein and Miss Carolyn Moore who capably handled many of the amine evaluations, analyses and preparations; to Mr. Ernest Gamble for assistance in the analytical methods; to Miss Jacqueline Fetsko for several ink preparations and for two of the figures; to Mr. Aubert Bibolet for ink preparations; and to Mr. Bern Malizia for preparation of the Calvin complexes. The typing of the final draft was done by Mrs. Marjorie Correll, whose efficiency compensated in part for many errors in the original manuscript.

The author has reserved last mention for the one person without whom the undertaking could not have been completed, and whose patience and self-denial have made the difficulties encountered in the past two years seem trivial. That person, who deserves far more credit than she ever will receive, is the author's wife, Hilma.

R. R. Myers

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CHAPTER 1

INTRODUCTION

Statement of the Problem

A long range program was started on June 1, 1950 for the purpose of studying the effect of complexing upon the catalysts used in the drying of oleoresinous vehicles.

Ever since the first accidental inclusion of oxides of lead in linseed oil, the use of metals as drying catalysts has been employed satisfactorily in the paint, varnish, and ink industry. In the form of soluble salts of organic acids, the divalent ions of manganese, cobalt, and lead have dominated drier technology for decades.

The supremacy of these conventional catalysts was challenged first by the discovery that certain complex compounds of iron, in which the metal is coordinately bound to nitrogen atoms in the organic part of the molecule, were of biological importance because of their ability selectively to catalyze oxidations under mild conditions (the role of hemoglobin in animal metabolism is an example). In view of the fact that iron normally is an oxidation catalyst only at high temperatures, the obvious conclusion that the type of bond peculiar to these complex molecules was responsible for the greater activity led early experimenters to a study of related compounds as driers for inks.

In the field of drier chemistry considerable confusion existed with regard to the use of complexes at the time this work was started. Consequently, a more concerted effort was planned in order to advance and systematize our knowledge of complex catalysts. More specifically, the program was designed to find either a substitute or an accelerator for conventional ink driers which would effect an improvement in drying as judged by the criteria of:

1. Drying rate - a necessary, but not a sufficient, criterion;
2. Availability - a prime consideration in view of wartime shortages of critical metals;
3. Cost - of equal importance, at least in times of normal supply of materials;
4. Color - generally of secondary importance, but an enigma in complex chemistry;
5. After-hardening - an undesirable condition encountered in the use of excessive metal, especially cobalt;
6. Oil-solubility - not generally a serious problem;
7. Aging - serious when manifest as loss of drying ability, precipitation of catalyst, or deepening of color;
8. Greasing - often encountered in lithography, and for which the drier sometimes is held responsible.

Also included in the original program was the goal of explaining the role of the catalyst in the oxidation of linseed oil, so that new driers could be made according to specification. In fact, the whole picture of the complex program as a means of procuring data of a fundamental nature hinged on the development of a satisfactory explanation of what happens when a complex forms. That considerable success has been achieved along the lines of fitting theory to practice will be evident from a reading of this dissertation.

History

The possibility that a more efficient metal drier could be developed was suggested by the work of biochemists who learned that compounds such as hemin and cytochrome C are capable of performing selective oxidations under the mild conditions encountered in living substances. Hemin, the functional part of the hemoglobin molecule, contains iron in a rather complex arrangement written as*:

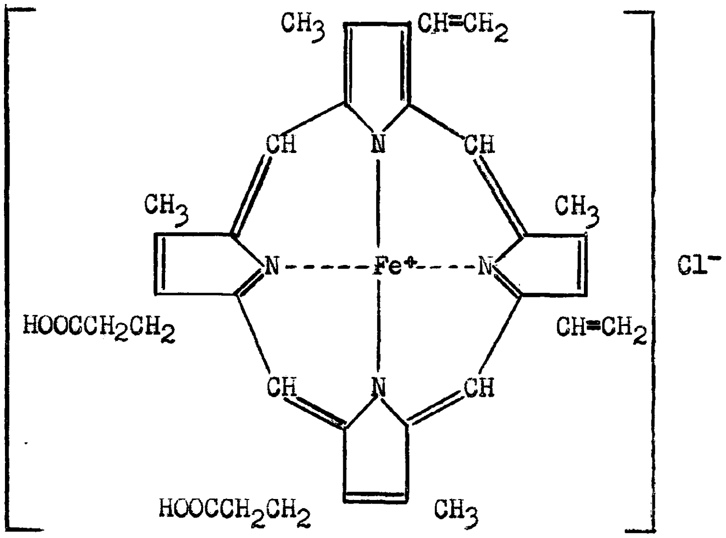

Figure 1. Hemin

while cytochrome possesses a structure similar to hemin in that coordinate covalent linkages between nitrogen and the central metal are present.

Because of the similarity between biochemical oxidations and the drying of linseed oil, the use of hemin in the oxidation of drying oils was tried as early as thirty years ago (132) in a series of successful experiments in which the catalyst was present in the form of an aqueous emulsion. An extension of the work (75), in which homogeneous solutions were used, at first was unsuccessful. Later, these same workers (76) found that hemin catalyzed the oxidation of

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* Reference 58, page 433.

linoleic and linolenic acids, but was destroyed in the process. Actually, the role of ferrous salts as oxygen carriers had been pointed out as early as 1857 (136).

Unfortunately, the active components of blood constitute less than two percentage of the solids content which, combined with recovery difficulties, has placed a prohibitive price on hemin as a catalyst. This would be a deterrent to its use even if it were not destroyed by the acid components of linseed oil.

Meanwhile, considerable headway was being made by Cook and his coworkers on the characterization of phthalocyanines. The effects of a complex iron phthalocyanine pigment on hydrogen peroxide decomposition (40a), on the oxidation of benzaldehyde (40b), on the conversion of olefins to carbonyl compounds (40c), and on chemiluminescent reactions (40d) were studied; with the result that the catalytic properties of complexed iron were demonstrated quantitatively on oxidations of widely varied nature. The behavior of driers during oxidation was studied (63) in terms of their oxidation products by Gardner.

These considerations led earlier investigators into a search for a simpler solution, in which complexes were synthesized around the central metal. In 1941, a synthetic complex was found which would influence biochemical processes in a fashion similar to the effect of hemin (118): the discovery was made that the oxygen absorption of phospholipids could be enhanced by an iron-orthophenanthroline complex. This immediately suggested the possibility of effecting economies in driers, with the result that one worker (113c) found that orthophenanthroline could be employed as a drier accelerator merely by adding it to a system already catalyzed by conventional driers.

While certain restrictions must be placed on the use of orthophenanthroline, it has been test-marketed by a large drier manufacturer* and can be regarded as the first step in a new drier technology. Chief among these limitations are the facts that it is useless with the most important conventional drier (cobalt), and that its cost exceeds the economies effected in many instances.

By the time the National Printing Ink Research Institute had become interested in the coordinated drier problem the need had become apparent for a fundamental approach to the problem. The literature (113,167) contains the claims that cobalt can be upgraded by the addition of orthophenanthroline, dipyridyl, and other amines; while attempts to effect the same phenomenon in the laboratories of the Advance Solvents Corporation (one of the sponsors of this work) were fruitless. Not only have the latter's results been supported by the findings of D. M. Nace (112,176) at Lehigh; he noted further that most amines, including those listed above actually were deleterious when used in conjunction with cobalt. Further vindication of the negative results has been afforded by the omission of cobalt from the patent claims (168) emanating from the work originally reported in reference 167.

Two facts remained which attested to the fruitfulness with which the attack on the problem had been initiated: certain amines were found which prevented excessive loss of drying on aging in certain pigmented vehicles, and the efficiency of iron in the form of its naturally occurring complexes had been reproduced in synthetic materials of comparatively simple structure. The reasons for both phenomena remained unexplained.

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* Activ —3, a product of the R. T. Vanderbilt Company.

Inasmuch as the loss of drying study had been carried to a satisfactory practical solution by Nace, the more basic problem of explaining activation via the complexing route was chosen for further study.

Coordinate Covalency

A clear concept of the role played by electrons in the establishment of a coordinate covalent bond is necessary for the understanding of what happens when a complex is formed; consequently, a considerable portion of this and succeeding sections is devoted to a discussion of electronic configurations. Chief interest centers around the so-called "d shell" of the metal ions taking part in the reaction of linseed oil with oxygen, but it is advisable to begin a discussion of coordination with more elementary concepts.*

The coordinate covalent bond was depicted in hemin (q.v.) as a dashed line--a convention which is used throughout this work. Frequently, the coordinate covalent link is denoted by an arrow to indicate which element has donated the pair of electrons used in bonding; but inasmuch as the metal ion is always the acceptor in the partnerships we shall study, the need for such clarity is not felt here.

Electronically, the coordination process can be viewed as the formation of a single bond from a pair of electrons originally associated with one of the participants. The simplest example is the formation of the ammonium ion by the capture of a proton by ammonia:

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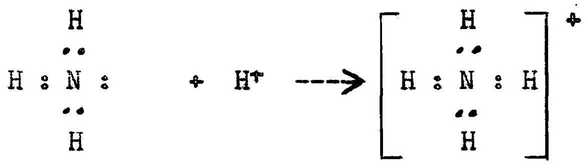
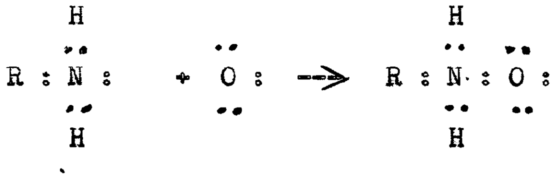
* For a more detailed discussion, the reader is directed to Reference 48, Chapter 1, and Reference 140, pages 109ff, 163ff, 204ff.



All four of the hydrogen-nitrogen bonds are identical, despite the fact that the first three were formed by ordinary covalency between nitrogen and hydrogen. The phenomenon called bond hybridization has taken place.

Similarly, in the formation of amine oxides via the electron exchange:



the nitrogen-oxygen bond is identical with the bond which would have been formed had the atoms contributed one electron apiece.

Utilizing the concept of atomic orbitals*, the picture of the formation of an amine oxide is as follows:

		<u>2s</u>	<u>$2p_x$</u>	<u>$2p_y$</u>	<u>$2p_z$</u>
Oxygen:	$2s^2$ $2p^4$	∘ ∘	∘ ∘	∘	∘
Nitrogen:	$2s^2$ $2p^3$	xx	x	x	x
N in RNH_2O	$2s^2$ $2p^6$	xx	xo	xo	xo
O in RNH_2O	$2s^2$ $2p^6$	∘ ∘	∘ ∘	∘ ∘	xx

For clarity, electrons contributed by carbon or hydrogen are indicated by open dots; those from oxygen, by closed dots; those from nitrogen, by crosses. From this legend the formation of an amine oxide is seen to result from the part time occupancy of the nitrogen 2s electrons in

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* Underlying orbitals, which do not participate in reactions, are omitted.

an oxygen 2p orbital. It is understood that all three p orbitals have the same energy requirements, and that either of the two unfilled p orbitals of oxygen can receive the incoming electrons from nitrogen. The ejected electron pairs up with an electron in the lowest-lying unfilled orbital: viz, the remaining p orbital.

Nomenclature

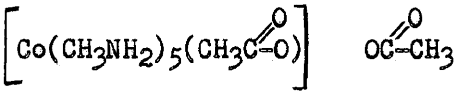
The naming of coordinate covalent compounds has been systematized by The International Union of Chemistry (86), whose conventions have been followed throughout this work. For the convenience of the reader, a brief discussion of the basic tenets follows.

Conventionally enough, the cation of an ionic compound is named before the anion. When the ion is complex, the name of the metal is embellished with prefixes denoting the coordinating groups, with ammonia of coordination appearing last in the sequence. Thus, the compound,

$$\left[Co(NH_3)_3(H_2O)Cl_2\right] Cl,$$

is named dichloroaquotriammine cobalt (III) chloride.

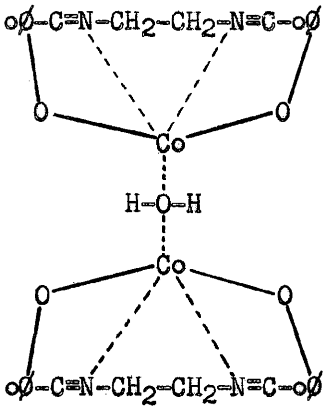
Generally, the prefixes end in the letter, o; but ammonia always is written as ammine (accented on the first syllable). Precedence has not been established on whether organic amines should be included in the category of ammine-formers; and if existing sentiment is not too far in favor of excluding all but ammonia from the group, a beginning is made here in the more general use of the term. In short, the convention used here is to name a compound of the type,



$$\left[\mathrm{Co(CH_3NH_2)_5(CH_3C(=O)\!-\!O)}\right]\quad \mathrm{OC(=O)\!-\!CH_3}\ ,$$

acetato pentakis (methylamine) cobalt (II) acetate; but the compound, itself, is a member of a group of ammines. The use of the Greek prefix is to denote a multiplicity of the group, itself, not of substituents within the group.

One further specific point must be mentioned: a bridging group is denoted by the Greek letter, μ . The example studied in the present work has the formula:



<u>Figure 2. Calvin's Complex</u>

and bears the name, bis(disalicylalethylenediamine)-μ aquo dicobalt (II). For brevity it is called Calvin's complex* and the organic portion is referred to as the Schiff's base.

Objectives

Originally, the program was outlined with four major objectives:

1. Replacement of cobalt in driers. Further impetus was given to this objective by increasing shortages of the metal.

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* References 21, 23, 31, 32, 33, 47b, 74, 80.

2. Reduction of cost. This has been of primary consideration since the inception of the work.

3. Improvement of solubility and color.

4. Development of a suitable theory of catalysis and a mechanism of drying.

The work was scheduled to be done in five distinct phases which consisted of the following:

1. Addition of amines and other drier aids to metal-catalyzed linseed oil.

2. Preparation of amine complexes of metals and their evaluation of driers.

3. Development of a suitable method of evaluation.

4. Characterization of complexes by a method which permits a correlation to be made between some physical property and reactivity with oxygen.

5. Development of a classification scheme whereby promising new complexing agents can be singled out for testing.

In effect, the plan outlined above represented a translation into action of the tentative agenda which emerged from the first technical conference with representatives of the two companies* which supported this work. These agenda are reproduced in Appendix I exactly as they were recorded at the first meeting.

---

* Harshaw Chemical Company and Advance Solvents Corporation.

CHAPTER 2

THEORETICAL

Electronic Configurations

When a metal forms an ionic bond, electrons are lost from the outlying s orbital of the metal and are transferred to the anion. Electronically, using cobalt as an example, the ionization can be represented as follows:

	3d					4s
Co	∘∘	∘∘	∘	∘	∘	∘∘
Co^{+2}	∘∘	∘∘	∘	∘	∘	

When coordination occurs the incoming pair of electrons can enter either one of the 3d orbitals or the 4s orbital. In all previously reported studies on coordination compounds no difficulty has been encountered in assuming that the structure has been built upon the ion as the foundation; however, the work covered by this dissertation is characterized by the necessity of considering the possibility that the central metal is bound covalently to the non-metal, which requires that the electronic configuration of the metal in CoX_2 be delineated. Inasmuch as the energy associated with the 4s orbital is less than that of any other unfilled orbital*, one is justified in selecting the 4s orbital as the source of one of the covalent linkages; the difficulty arises in picking the second orbital used by the divalent metal in forming the second covalent bond. Normally, one would be inclined to cast one of

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* There are very important exceptions, as pointed out in Chapter 7, which confine this discussion to the elements from manganese to nickel.

the 3d orbitals in this role; but until magnetic susceptibility data* to the contrary are supplied, the author contends that the rules** of spectroscopy apply during the formation of the covalent bond. If so, the 4s electron which is ejected at the time of covalent bond formation cannot enter any orbital except a p orbital, since the azimuthal quantum number of this orbital differs from that of the s orbital by unity.

From these considerations, the picture of covalent bond formation does not differ appreciably from the ionization shown on the preceding page. An additional group of orbitals is required, however, to show the destiny of the ejected 4s electron:

	3d					4s	4p		
Co	••	••	•	•	•	••			
CoX_2	••	••	•	•	•	•○	•○	__	__

The open dots represent electrons contributed by the non-metal; the underscored orbitals are vacant.

A definite stereochemical pattern*** is imposed upon the molecule by the sp hybridization shown above, with the result that so long as the metal eschews reduction to a lower valence that structure will persist in which the participation of these two orbitals is required. The so-called ionization which occurs when the metal salt is dissolved in water is in reality a dissociation in which the non-metal is replaced by water and permitted to wander as the anion. The cation in this case is the hydrated metal ion. The sp bond hybridization has not been changed.

---

* These show the number of unpaired electrons in the molecule.

** Specifically: the azimuthal quantum number can change only by unity.

*** The bonds will be directed at approximately 180° angles. See reference 121.

Now if coordination occurs, the first pair of electrons enters one of the half-filled 3d orbitals, forcing its occupant into an adjacent 3d orbital. The next pair of electrons likewise will enter a 3d orbital, but in this case the only available orbitals capable of accepting the ejected electron are in the 4p subshell. One more addition of electrons can occur before the next higher subshell (the 5s) must be brought into the picture. In all, four complexing groups can be accommodated.

The above view is a departure from the conventional representation of the formation of complex ions. If the electronic structures of the six possible coordinated species of the cobalt ion are written*, the electron lability can be seen to range from extreme willingness to leave the coordination entity to moderate reticence:

Table I

ELECTRONIC CONFIGURATIONS OF COMPLEXED COBALT IONS

	3d					4s	4p			5s
Co^{++}	oo	oo	o	o	o					
$Co(A)^{++}$	oo	oo	oo	o	xx					
$Co(A)_2^{++}$	oo	oo	oo	xx	xx	o				
$Co(A)_3^{++}$	oo	oo	oo	xx	xx	xx	o			
$Co(A)_4^{++}$	oo	oo	oo	xx	xx	xx	xx	o		
$Co(A)_5^{++}$	oo	oo	oo	xx	xx	xx	xx	xx	o	
$Co(A)_6^{++}$	oo	oo	oo	xx	xx	xx	xx	xx	xx	o

A d electron in the monoammine will have a slightly greater tendency to be lost than in the uncomplexed species owing to the reduction in the effective charge of the cobalt ion. The diammine and hexammine are powerful reducing agents because of their possession of a single s electron (as found in the alkali metals), and tend to lose the

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* Reference 48, page 176.

third electron irreversibly. The triammine would be a strong reducer; the tetrammine, considerably less; and the pentammine would behave somewhat as a halogen, since it possesses a nearly complete p shell. These views can be traced to the work of Sidgwick (140).

The same treatment applied to covalently bound cobalt results in the following picture of complexing:

Table II

ELECTRONIC CONFIGURATIONS OF COVALENT COBALT COMPLEXES

	3d	4s	4p	5s
CoX_2	∘∘ ∘∘ ∘ ∘ ∘	∘O	∘O	
$Co(A)X_2$	∘∘ ∘∘ ∘∘ xx ∘	∘O	∘O	
$Co(A)_2X_2$	∘∘ ∘∘ ∘∘ xx xx	∘O	∘O ∘	
$Co(A)_3X_2$	∘∘ ∘∘ ∘∘ xx xx	∘O	∘O xx ∘	
$Co(A)_4X_2$	∘∘ ∘∘ ∘∘ xx xx	∘O	∘O xx xx	∘

x denotes electrons from the ligand, A; o denotes electrons from group, X

The chief point of departure from the conventional picture concerns the diammine, for here no reason can be advanced to postulate extreme lability for the unpaired 4p electron. The species with the labile electron is now the tetrammine.

Formation of a pentammine or a hexammine would require the opening of a 5p orbital. This is not likely, since the rare gas* structure of argon already has been exceeded with the formation of the tetrammine, and no additional coordination positions are available. The striving for the rare gas structure can be advanced as the reason for the extreme lability of the 5s electron in the tetrammine.

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* Reference 48, page 172.

Redox Potentials

That coordination has an effect on electron affinity has been demonstrated by redox potential measurements (90). In fact, the orthophenanthroline complex of ferrous iron is used in oxidimetric titrations as a redox indicator, whereas the uncomplexed ferrous ion is too readily oxidized for this purpose. The magnitude of the displacement of the redox potential of the ferrous-ferric ion couple is shown in Table III, along with similar data for other complexes. These data were obtained from Reference 48, page 153. A high positive value indicates stabilization of the lower valence.

Table III

EFFECT OF COORDINATION ON REDOX POTENTIALS

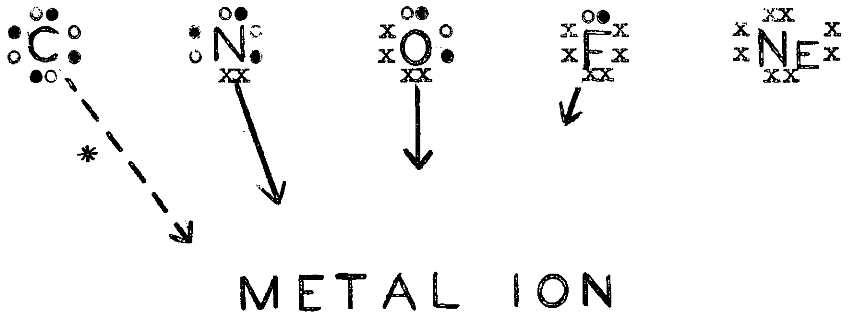
Equilibrium	Redox Potential
Co^{+2} --- Co^{+3}	+ 1.8 v.
$Co(CN)_6^{-4}$ --- $Co(CN)_6^{-3}$	- 0.8
Fe^{+2} --- Fe^{+3}	+ 0.74
$Fe(CN)_6^{-4}$ --- $Fe(CN)_6^{-3}$	+ 0.49
$Fe(oph)_3^{+2}$ --- $Fe(oph)_3^{+3}$	+ 1.14

Later, an effort will be made to show that redox potentials may be the best possible means of evaluating complex driers.

Complexing Periodicity

A characteristic of the periodic table is that those elements possessing the fewest valence electrons exhibit the greatest tendency to lose one or more electrons. The ionization potential of sodium is much less than that of magnesium; which, in turn, is exceeded by aluminum.

A similar phenomenon is manifest in coordination tendency. If the elements, beginning with carbon, are arranged according to their tendency to coordinate, the pattern follows their order in the periodic table:



(length of arrow indicates relative strengths of bonds)

Figure 3. Complexing Periodicity**

Carbon normally finds itself satisfied with four covalencies; however, its position to the left of nitrogen is warranted by the chemical behavior of certain compounds whose reaction intermediate is postulated to be a carbanion (carbon anion). The carbanion is so unstable that it is formed only in compounds capable of providing a redistribution of the excess electrons on the carbon to an element occupying a position to the right of carbon in the periodic table (2). Thus, ~~acetoacetic~~ malonic ester can produce a carbanion because it can be written as a resonance hybrid of three forms, two of which require oxygen to carry the negative charge:

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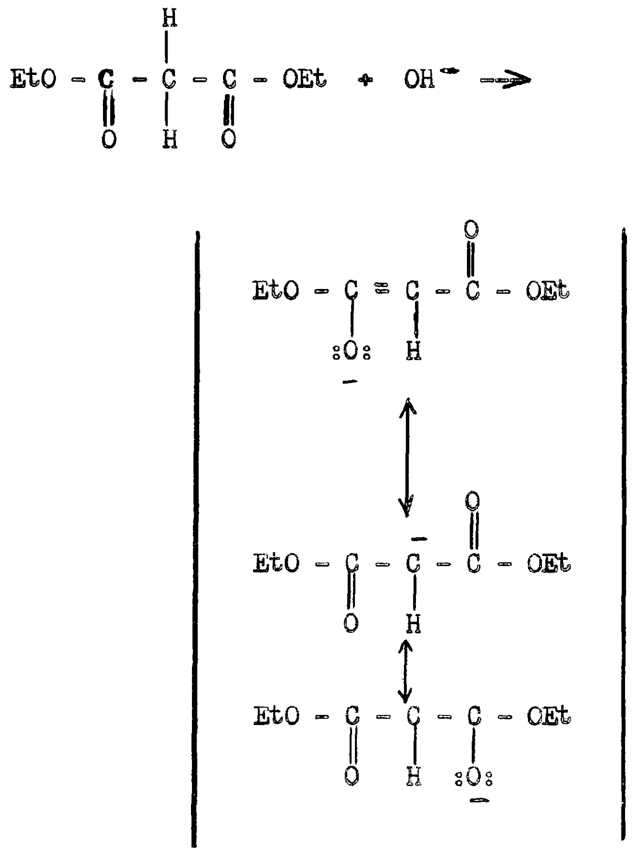
* Unknown for tetravalent carbon. See next paragraph.

** o: Shared electron contributed by element in question.
●: Shared electron contributed by H or R group.
x: Unshared electron. Only these are available for coordination.



$$EtO-\underset{\underset{O}{\parallel}}{C}-\overset{H}{\underset{H}{C}}-\underset{\underset{O}{\parallel}}{C}-OEt + OH^{-} \longrightarrow$$

$$\left|\begin{matrix} EtO-\underset{:\bar{O}:}{C}=\underset{H}{C}-\overset{O}{\overset{\parallel}{C}}-OEt \\ \updownarrow \\ EtO-\underset{\underset{O}{\parallel}}{C}-\underset{H}{\bar{C}}-\overset{O}{\overset{\parallel}{C}}-OEt \\ \updownarrow \\ EtO-\underset{\underset{O}{\parallel}}{C}-\underset{H}{C}=\underset{:\bar{O}:}{C}-OEt \end{matrix}\right|$$

The ability of carbon to coordinate with metals has been demonstrated (37,38) with olefins, and a study of the phenomenon would have enormous theoretical interest. Nevertheless, prior art in the field of complex driers has indicated that amines promised a more fertile field for investigation, and that the role of the surplus* electrons in olefins was explainable only by a treatment not amenable to the atomic orbital theory (45) used throughout this work.

Nitrogen is the first element of the group capable of contributing a pair of electrons over and above its full complement of covalent linkages. Just as the first ionization potential of the

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* Called π electrons.

alkali metals is the lowest of all the members of a given period, so are the elements of the fifth group the most active in coordination. Next in order of reactivity are the elements of the sixth group, whose two pairs of unshared electrons are reminiscent of the divalent alkaline earths. Here are found oxygen and sulfur.

The analogy can be extended further upon consideration of the capacity of an element for coordination. While sodium reacts with water much more readily than magnesium, its hydrogen-liberating capacity is only half as great. Similarly, an aliphatic amine will coordinate more readily with a metal ion than will the corresponding alcohol, but the alcohol conceivably will coordinate with two ions. An example is given in the section on nomenclature of a water bridge operating between two cobalt ions.

Fluorine, with its six exposed electrons, has only a slight tendency to coordinate, despite its threefold capacity for doing so. Neon, with eight electrons, does not coordinate at all.

The periodicity which accompanies the tendency of normally covalently bound elements to coordinate is no anomaly of nature as would appear at first glance. One can predict that nitrogen and phosphorus compounds will be the strongest complexing agents, and that oxygen and sulfur compounds will be less effective.

Superimposed upon the effect of the electronic configuration are two factors which may amplify or mitigate the complexing tendency: one of these factors is the inductive or mesomeric effects of the organic constituent, which alter the basicity of the functional group; the other is the possibility of chelation which arises when a second functional group is present, albeit another nitrogen atom or a covalent bond former.

Viewed in this light, the purpose of the present study was to discover the optimum combination of structural effects in the synthesis of a complex drier, and to delve into the mysteries behind the phenomenon.

Related Theoretical Developments

Pertinent information has been obtained from theoretical developments in fields outside the domain of this work. The work of Pauling on bond hybridization has been mentioned. His concept of quantum mechanical resonance (123) has been employed in explaining the mechanism of linseed oil oxidation, while H. S. Taylor has been able to explain related phenomena by comparing bond strengths à la Pauling (121). Bailar (10-20), whose elucidation of the stereochemistry of complexes could be used as the basis of an independent investigation, has been a valuable source of background information. Biltz (27), whose measurements of vapor pressures marked a milestone in studies of the extent of complexing, has come the closest of any of the masters to providing fundamental data which could be applied directly to the solution of the linseed oil problem. Diehl (46,47) has forged an additional link between biological oxidations and linseed oil drying. Farmer* has provided virtually all of our present knowledge on the mechanism of drying which is discussed in the next chapter.

Application of the electronic theory (140) to coordination compounds has been made by Lowry (94), Smith (154) and Spiers (156), who, through a running controversy, brought to light the possibility

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* See References 49-55.

that the stability of chelate rings may be due to the formation of conjugated rings. This, combined with the striving of the metal ion for the rare gas structure, constitutes practically all of the driving force in the establishment of complexes.

CHAPTER 3

OXIDATION OF LINSEED OIL

The Problem

A clear-cut picture of the process selected for study is absolutely necessary in order for the fundamentals of the reaction to be appreciated. Ideally, the starting material in the study would be a purified ester such as methyl linoleate; the test method would consist of a physical means of measuring the rate of oxygen uptake or of determining changes in the substrate on oxidation. Since oxidation is followed by polymerization, one approach would be to determine molecular weights as a function of time with various catalysts. In effect, the test method described in Chapter 4 is based on that principle, despite the fact that the results must be expressed empirically.

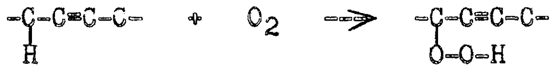
One major assumption was made at the outset of the work which, admittedly, is challengeable: the rate-controlling step in drying is considered to be the initial oxidation; and, as such, it is affected by oxidation catalysts rather than by polymerization accelerators.

The reasons for the uncompromising stand on the reaction kinetics are that 1) oxidation catalysts, and not polymerization catalysts, are active; 2) the oxidation step has been studied in detail and found to have a long induction period; 3) the polymerization rate has been shown (49c,f) to depend on the intermediate formed from the oxidation step; 4) oxidative breakdown of cross-linked films is accelerated by the drying catalyst.

Mechanism of Drying

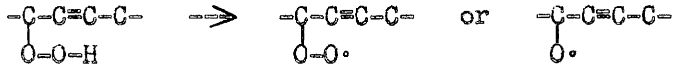
In a series of reports Farmer (49-55) has arrived at the now undisputed conclusion that the drying of linseed oil proceeds through the following steps:

1. Hydroperoxide formation:



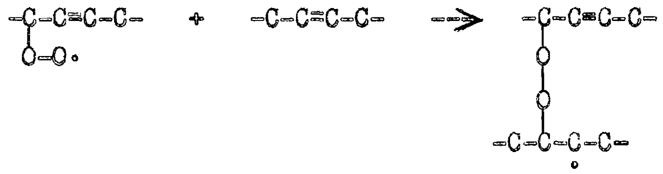
$$-\underset{H}{\underset{|}{C}}-C=C-C- \;+\; O_2 \longrightarrow -\underset{O-O-H}{\underset{|}{C}}-C=C-C-$$

2. Hydroperoxide breakdown:



$$-\underset{O-O-H}{\underset{|}{C}}-C=C-C- \longrightarrow -\underset{O-O\cdot}{\underset{|}{C}}-C=C-C- \quad \text{or} \quad -\underset{O\cdot}{\underset{|}{C}}-C=C-C-$$

3. Cross-linking:



4. Oxidative breakdown of the cross-linked polymer.

The last mentioned step occurs on aging of the dried film. It is of concern to us only in that it adds impetus to the search for an improved catalyst; for it arises from post-drying oxidation of the polymer, and this is promoted by excess catalyst.

Numerous other explanations of the drying process have been advanced* but all are empirical and are based more on conjecture than on an interpretation of experimental results, as were Farmer's conclusions.

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* See References 63, 93, 103, 111, 113, 133, 155, 163, 167, 171, 174.

Role of the Drier

There are five possible ways in which a drier can shorten the drying time of an oleoresinous film (103):

1. The induction period of the hydroperoxide formation may be shortened by counteracting antioxidants in the vehicle;
2. The rate of oxygen absorption by the vehicle may be accelerated;
3. Gelation of the film may be made to occur at a point of lower oxygen absorption;
4. The maximum quantity of oxygen absorbed may be decreased;
5. A combination of the first four effects may occur.

Naturally, a wide divergence of opinion exists concerning why a catalyst is operative. The chief controversial point is whether the drying rate is determined by the oxidation or the polymerization step (113a).

Explanation of Alpha Methylenic Reactivity

One satisfactory explanation of the reactivity of the alpha carbon atom is based on Pauling's concept of resonance forms (123). According to this quantum mechanical view, if a reaction can proceed through two different intermediates, that intermediate is favored for which the most resonance forms can be written. Thus, the reactive portion of the unsaturated fatty acid found in linseed oil is the alpha carbon; for when a hydrogen is lost from that carbon, not only are there two possibilities for loss of the atom, but also two resonance forms exist for each possibility owing to the potentiality for migration of the double bond:

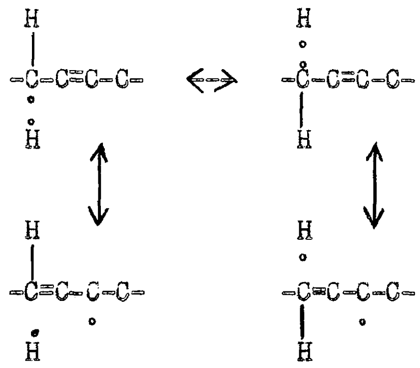
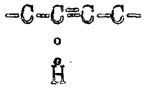


Figure 4. Resonance Forms of the Alpha Methylenic Radical

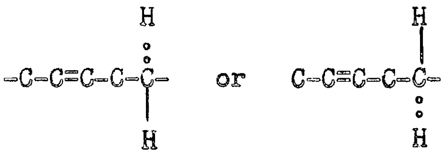
Now if the hydrogen is lost from the doubly bound carbon, then



$$-C-\underset{\substack{\circ\\H}}{C}=C-C-$$

is the only form available.

If the hydrogen is lost from a carbon atom not conjugated with the double bond, there are no resonant forms although two possibilities exist in many cases:



$$-C-C=C-C-\overset{\substack{H\\\circ\\\circ}}{\underset{\substack{|\\H}}{C}}- \quad \text{or} \quad C-C=C-C-\overset{\substack{H\\|}}{\underset{\substack{\circ\\\circ\\H}}{C}}-$$

From these considerations one would expect the fatty acid free radical which forms from the loss of an alpha methylenic hydrogen to be the most stable of all the possible intermediates in the oxidation process.

Drying Variables*

The most influential variable in the drying of unpigmented linseed oil is the catalyst concentration. Exhaustive studies performed by Albert Walker (164) have produced an equation of the form,

$$y = \frac{a}{x} + b \quad ,$$

which was shown to hold for the drying time isotherms of cobalt-catalyzed ASTM linseed oil (the standard formulation being 0.03% cobalt). The ordinate, y, represents drying time; x, the percentage metal; at 80°F., $\frac{a}{x}$ has the value 0.06 hours divided by the percentage metal; and b, the limiting drying time at infinite concentration of metal, equals 2.0 hours.

Figure 5 is an isotherm constructed from the relationship,

$$t = \frac{0.06}{\%\ \text{metal}} + 2.0 \quad ,$$

for the purpose of illustrating two apparent anomalies which will enter into the discussion to follow on amine additives. The first is that the evaluation of a metal at a concentration where its activity equals or exceeds 0.03% cobalt is less accurate than at lower concentrations owing to the difficulty of measuring drying time differences of the order of magnitude of fractions of an hour. The second is that an additive will not appear to exert as great an influence on drying characteristics when tested in the flattened right hand portion of the curve, even if precise measurements were possible.

At a given catalyst concentration the most important variable is the temperature. A logarithmic relationship has been found (164)

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* See References 69, 93, 113b, 133, 155, 162, 163, 164, 171, 173.

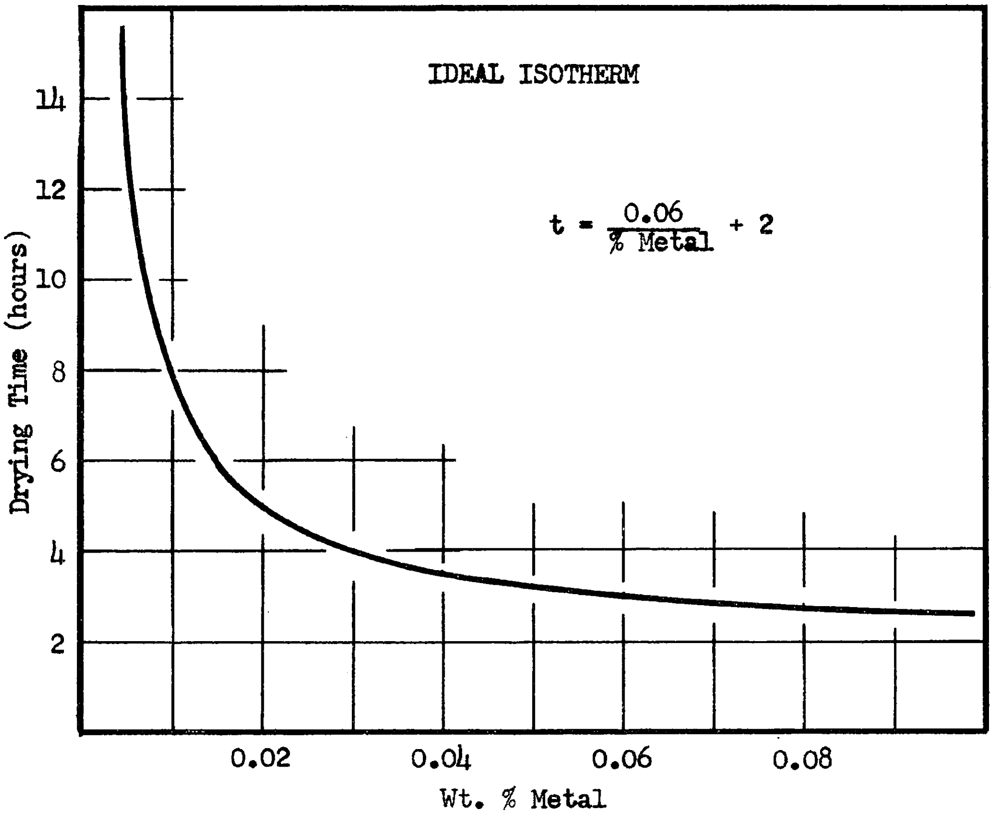

Figure 5.

Effect of Catalyst Concentration

between drying time and temperature, but the data are best presented on a linear scale as in Figure 6, for in this form they can be used to select drying time values at various cobalt concentrations and temperatures. The relationship between these curves and the ideal isotherm of Figure 5 is apparent if one recalls that the family of curves differs only in the slope constant in the equation $y = \frac{a}{x} + b$. Note that the constant, b, remains at 2 hours, regardless of temperature.

A third variable requiring careful control is the nature of the vehicle. A series of tests, performed with various raw and refined linseed oils in connection with the study reported in Chapter 4, demonstrated that the oil plays an important role in evaluation results. With this one exception, all studies were made using the standard vehicle described in Chapter 4.

Humidity, light intensity, air flow, film thickness, and nature of the substrate all influence evaluation results to a greater or lesser extent. All except the first mentioned were controlled carefully throughout the investigation.

Because of certain results reported in Chapter 5, the role of water in drier activity is believed to be the formation of microscopic voids in the surface, thereby increasing the area exposed to oxygen. This explanation also accounts for the retardation of drying by high humidity.

Along similar lines, the activity of complexes containing volatile amine groups might be considered due to steady evaporation of the amine which would leave behind not only voids in the vehicle, but also nascent uncoordinated positions on the central atom.

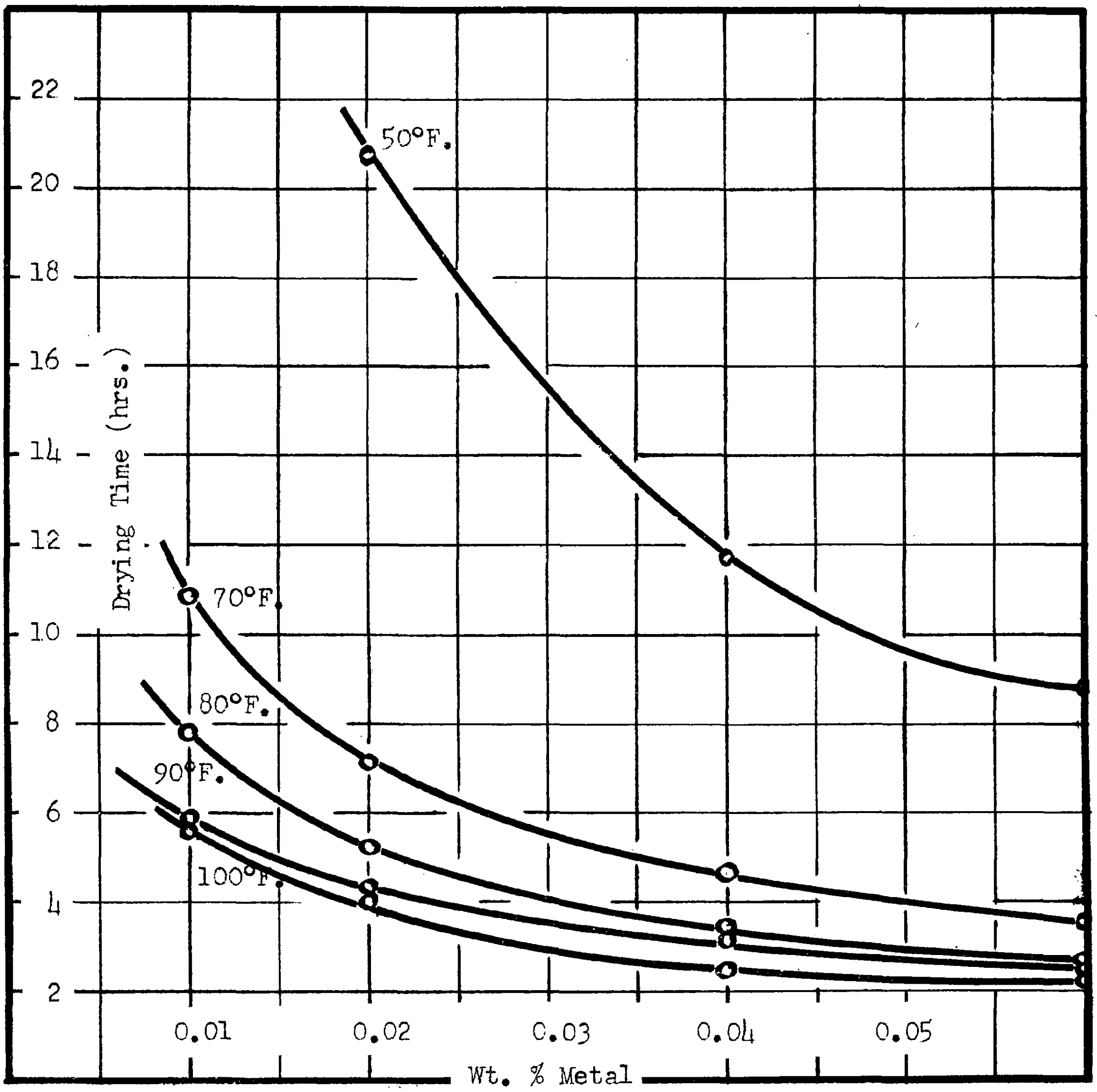

Figure 6

<u>Drying Time Isotherms</u>

G.E.
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CHAPTER 4

AMINE EVALUATION

Metals Employed

Originally intended as a project to increase the effectiveness of cobalt catalysts, the chief concern of this aspect of the problem soon became the discovery of a substitute for that "indispensable" (111) metal.

Of over 150 amines tried in a molar ratio of 2:1 with five different metals, only six were found which gave any indication whatsoever of assisting cobalt in its catalysis of linseed oil drying; in no case did the acceleration exceed 20%. Theoretical considerations presented shortly, indicate that drastic acceleration of cobalt cannot be achieved.

Contrasted with these results are the phenomenal drying rates found with complexes made from the addition of numerous amines with manganese and iron. The findings reported later in this section are of considerable practical value in that they have delineated the course of action which must be followed in advancing the new drier technology, and of theoretical interest in view of the pattern established by the effective amines and the interpretation of this pattern in electronic terms.

Iron and nickel were included in the group of metals out of theoretical interest. Iron, of course, offers the sort of combination of low cost and ready availability which prompts one to examine it thoroughly from a practical standpoint as well. Lead was included in the list purely because of practical aspects.

Classification of Complexing Agents

The oxidation of linseed oil having been reduced to a situation in which the efficacy of the catalyst constituted the only variable, a means of describing the agents used to effect the changes in the catalyst was desired. The classification scheme given as Table IV was designed to permit a listing of all amines studied, or planned for study, in a numerical sequence based on similarities of structure. Examples of the use of the classification scheme are given in Appendix II which lists all of the amine additives used in the current investigation.

Equipment

Wholesale evaluation of films containing various types of driers required an apparatus capable of recording drying times while unattended. The Gardner drying time recorder shown in Figure 7 was selected for the purpose; and, with the exception of one series of evaluations performed according to another group of specifications*, was employed throughout this work.

The Gardner apparatus consists of a Bakelite dolly 29"x4" equipped with casters at either end, and directed by a metal guide to progress horizontally at a rate of three centimeters per hour by means of a rack engagement to a synchronous motor. Clamped to each dolly is a pair of plate glass slides, 27"x1", containing the film to be evaluated, and passing beneath a 5" gear whose impression is left on the film.

Constant temperature, light intensity, and air flow were

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* See Appendix III

Table IV

CLASSIFICATION OF DRIER AIDS

Three digits are employed to classify the amines used as accelerators. Other compounds or amines containing functional groups require one or more additional digits which are separated from the classification digits by a decimal.

A. Nitrogen Configuration

0.	None	0 - - . -
1.	Primary amine	1 - - . -
2.	Secondary amine	2 - - . -
3.	Tertiary amine	3 - - . -
4.	Quaternary ammonium	4 - - . -
5.	Other	5 - - . -

B. Carbon Character

1.	Aliphatic	1 - . -
2.	Aromatic	2 - . -
3.	Alicyclic	3 - . -
4.	Heterocyclic	4 - . -
5.	Carboxyl	5 - . -
6.	Other	6 - . -

C. Coordination Multiplicity

1.	Monodentate	1. -
2.	Bidendate	2. -
3-9.	n Dentate ($n < 10$)	3. etc.

D. Constituents

0.	C, H, N only	.0
1.	Containing oxygen (ethereal, hydroxyl)	.1
2.	Containing sulfur	.2
3.	Containing halide	.3
4.	Containing metals other than the coordinating metal	.4
5.	Containing carboxyl	.5
6.	Containing other substances	.6
7.	Containing unsaturation	.7

For examples see Appendix II.

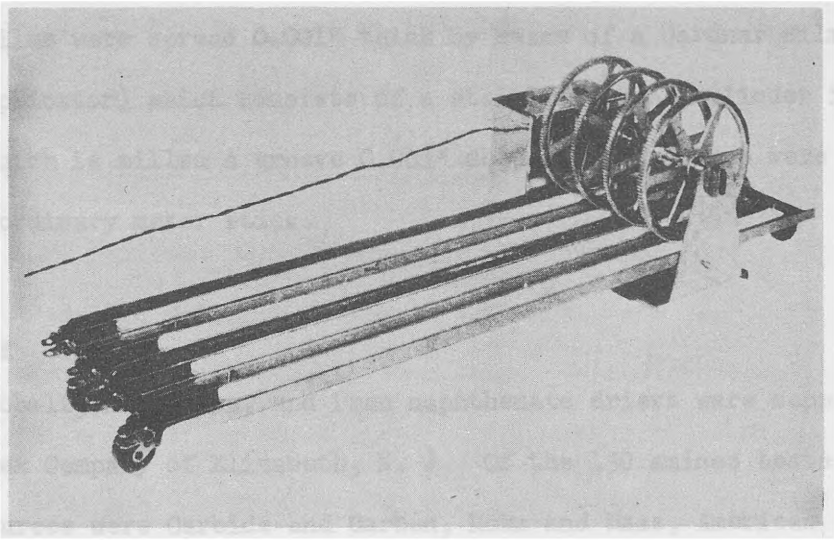

Figure 7

Gardner Drying Time Recorder

maintained by a plywood cabinet equipped with a 15-watt fluorescent lamp mounted horizontally and transversely over the dolly at a point preceding its passage under the gear, a deKhotinsky thermoregulator assembled in series with a 750-watt radiant heater mounted inside a perforated metal container. Air was supplied by a small centrifugal blower mounted outside the cabinet at a linear velocity of 160 cm./min.

Films were spread 0.001" thick by means of a Gardner Film-o-graph (Budd applicator) which consists of a stainless steel cylinder in one end of which is milled a groove 0.001" deep. Drying times were read with an ordinary meter stick.

Materials

Cobalt, manganese, and iron naphthenate driers were supplied by the Nuodex Company of Elizabeth, N. J. Of the 150 amines tested, the chief sources were Carbide and Carbon, Rohm and Haas, American Cyanamid, Tennessee Eastman, Monsanto, Armour, Sharples, Alrose, and Harshaw Chemical Company. The important class of Schiff's bases was prepared in the laboratory according to directions given in Reference 8.

The linseed oil was purchased in a 50-gallon lot from Archer-Daniels, Midland Company, and meets ASTM specifications #D 234-48 (Appendix IV).

Standards

A standard concentration was set for each metal studied as well as for a few not covered by this report. The standards are given in Table V.

Table V

STANDARD METAL CONCENTRATIONS

Metal	Standard Concentration (Wt. % Metal)
Cobalt	0.03
Manganese	0.05
Iron	0.05 or 0.10
Lead	0.30
Nickel	0.05
Calcium	0.10
Zinc	0.10
Chromium	0.10
Rare Earths	0.06

The standard vehicle was ASTM raw linseed oil (Appendix IV). The anion* was the naphthenate for amine studies; and the 2 ethyl hexoate, oleate, chloride, or acetate for complexes. Screening tests on amines were made at a 2:1 molar ratio based on the metal; succeeding tests on the more promising amines were made at lower ratios as indicated in the individual tabulations of results.

Procedures

The test method consisted of reading the times of the three characteristic gear impressions made upon the film as it dried. The first of these, the so-called Drop Time, occurred when the thread of material breaking away from the departing tooth of the wheel had become sufficiently rigid to prevent a small drop from forming in the center of the wheel impression. The second, called Dry Time, which invariably followed the first by one hour or slightly less, occurred when the entire tooth impression no longer penetrated the film. The third, or Dry Hard

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* The anion has a pronounced influence on results. See References 63, 78, 109.

Time, was attained when no impression whatsoever was left by the wheel.

Of the three characteristic impressions, the most desirable from the standpoint of measuring the tack-free condition of the film is the Dry Hard Time. Unfortunately, this impression was incapable of being read reproducibly; consequently, the easily read, readily duplicated Drop Time was adopted as the measure of the time of drying. All references to drying time in this report are understood to mean the Garnder Drop Time.

In the case of ink films the problem of selecting the drying time was not encountered, for in these studies the gear was covered by a cylinder made from adding machine paper, and the characteristic impression occurred when the ink no longer offset onto the paper.

Cobalt analyses were performed according to the method of E. Gamble (62a), in which the metal was removed from the organic medium by successive extractions with concentrated hydrochloric acid, and the blue coloration of $CoCl_2$ measured with a Coleman spectrophotometer. Alternative analyses which were considered when this method was found to fail for complexes, but which had not been developed at the time complexing studies on cobalt were abandoned, were the nitroso R salt method, the alpha nitroso beta naphthol method, and ashing.

Manganese analyses were performed spectrophotometrically by the method of Gamble (62b), and also by ashing. The spectrophotometric method required an excessive amount of labor owing to the necessity of converting the manganese into the permanganate form after removal of all organic material; and as a consequence, an alternative method was tried. The best method required only the addition of concentrated sulfuric acid to the complex contained in a porcelain crucible and repeated evaporation to dryness, after which the manganese sulfate was dried in the crucible by gentle heating with a soft Bunsen flame. In effect, this method was a variation of the ashing procedure which could not be used owing to uncertainties which existed concerning the oxide of manganese which resulted from ignition.

Amine addition was conducted according to a carefully organized plan in which each amine was dissolved separately in 20 ml. of ASTM linseed oil. At first solutions containing 17×10^{-5} moles of additive per milliliter of linseed oil were made in order that additions to 0.01% cobalt (17×10^{-7} moles/ml.) could be made with an insignificant reduction in metal concentration. With the establishment of 0.03% cobalt as the primary standard for all of the metals, the technique was altered as follows:

Whenever possible, solutions containing 0.0034 moles of amine per 80 ml. of ASTM linseed oil were made. Stock solutions of each metal in the same vehicle were prepared at twice the standard concentration. Blending was done in 12 ml. tubes by pipetting exactly 5 ml. of the metal stock solution, a quantity of amine solution calculated to produce a 2:1 molar ratio of amine to metal, and the amount of linseed oil required to bring the total volume to 10 ml.

Method of Reporting Results

With the adoption of 0.03% cobalt as the standard, results were expressed in terms of gamma values. By dividing the drying time of 0.03% uncomplexed cobalt by the time required for the complex formulation to dry under identical conditions, a figure was obtained which was expressable to the second decimal point, and to which the term, gamma

(γ), was assigned owing to its similarity to the relationship between activity coefficients in thermodynamics.

A high gamma value signifies a more potent catalyst than a low one. In studying cobalt complexes a γ exceeding unity indicates an improvement; in the case of other metals whose γ is less than 1.00 when uncomplexed, a lower gamma value may still represent considerable improvement, and the value, $\gamma = 1.00$, carries no special significance.

For theoretical treatment of the data, the value, $\gamma = 1.00$, has some significance: in a later chapter the possibility of improving a manganese or an iron catalyst to a point which is unattainable with cobalt in any form is discussed; and since gamma values for cobalt complexes rarely exceed unity by a wide margin, the occurrence of high gammas with other metals represents an achievement of both practical and theoretical importance.

In the case of manganese, gamma values based on a manganese control (0.05% conventional manganese drier) are listed frequently in addition to gammas based on 0.03% cobalt. Whenever this is done, an explanatory note accompanies the values in order to avoid a misinterpretation of the results.

Results of Preliminary Screening of Amines

Earlier data were reported graphically until the magnitude of the effort became greater than the benefits derived therefrom. By operating at a range from two to six moles of amine per metal atom, the observation was made that effects were as measurable at the lower concentration as at the high (at least in the case of active amines--see Appendix V).

All results given in Table VI were determined at the standard metal concentration* at a molar ration of 2:1 (amine to metal). The standard temperature for the experiments was 90°F., in which case the control film was dried at the same temperature.

Table VI

EVALUATION OF AMINE DRIER ADDITIVES

Type	No.	Results : γ .03 Cc				
		Cobalt *	Manganese	Iron	Nickel	Lead
014.1	87	0.70	0.70	0.30	<0.2	0.35
022.15	144	1.00	0.31	<0.14		
030.1	131	0.95	0.29	0.18		
111.0	1	(1.0)				
	2	(1.0)				
	3	(1.0)				
	4	(1.0)				
	23	(1.0)				
	25					
	26	(1.0)	0.50	0.30		0.30
	36	(1.0)	0.50			
	135	1.07	0.58	0.18		
111.1	86	0.70	0.75	0.30	<0.2	0.35
	129	0.60	0.96	0.18		
	130	0.70	0.69	0.21		
111.15	46	(1.0)	0.50	0.20	<0.2	0.50
	1G	(0.9)	0.59	0.33	<0.2	
	2G	(0.9)		0.32	<0.2	
	3G	(0.9)	0.69	<0.2	<0.2	
	6G	(0.7)	0.64	<0.2	<0.2	
111.52	5G	(0.8)	0.66	<0.2	<0.2	
111.7	37	(1.0)	0.40	0.35		0.30
112.0	137	0.75	0.69	0.21		
112.2	53	(1.0)	0.50		<0.2	0.60
112.52	4G	(0.9)	<0.24	<0.2	<0.2	
113.0	133	0.90	0.43	0.23		
121.0	15	(0.9)	0.50	0.30		0.30
	79	1.00	0.90	<0.2	<0.2	0.30
	80	0.40	0.50	0.30	<0.2	0.35
121.12	145	1.02	0.58	0.17		
121.5	84	0.90	0.60	<0.2	<0.2	0.35
122.0	16	(0.6)	0.60			
	38	(0.8)	0.40	0.35		0.35
	65	1.00	0.40		<0.2	0.40
131.0	78	1.00	1.00	0.30	<0.2	0.35
131.17	99	0.85	0.55	<0.2	<0.2	<0.3
	100	0.75	0.60	<0.2	<0.2	0.30

* Parenthetical values obtained at 0.01% Co.

(continued)

Table VI (Cont'd)

Type	No.	Results : γ.03 Cc				
		Cobalt*	Manganese	Iron	Nickel	Lead
142.0	20	(1.0)	0.30			
	97	1.05	0.80	< 0.2	0.23	0.35
143	21	(1.0)	0.70	0.30		0.30
152.1	92	1.05	0.55	0.30	< 0.2	0.50
152.25	4H	(1.0)		0.32	< 0.2	
154.0	128	0.50	0.41	0.20		
154.07	132	0.80	0.91	0.38		
211.0	5	(0.9)				
	6	(0.9)				
	35	(1.1)	0.40	0.30		0.40
	81	1.00	0.50	0.30	< 0.2	0.30
	82	0.85	0.60	< 0.2	< 0.2	0.35
	140	1.00	0.50	0.17		
211.1	98	0.75	0.65	< 0.2	< 0.2	0.30
211.15	10	(0.9)	0.40	0.30		< 0.3
211.2	119	0.64	0.25	< 0.2	< 0.2	
211.5	139	0.70	0.69	0.14		
212.27	M4		0.55		< 0.2	
213.0	133	0.90	0.43	0.23		
	M5		0.76		< 0.2	
213.07	108	0.84	0.60	0.30	< 0.2	0.35
21n.0	3H	(0.8)	0.90	0.32	< 0.2	
221.0	28	(0.5)	0.30	0.20		< 0.3
	29	(0.2)	0.50	< 0.2		
	63	0.80	0.30		< 0.2	
	81	1.00	0.50	0.30	< 0.2	0.30
	82	0.85	0.60	< 0.2	< 0.2	0.35
	140	1.00	0.50	0.17		
221.1	30	(0.6)	0.20	< 0.2		< 0.3
	31	(0.3)	0.30	< 0.2		< 0.3
	98	0.75	0.65	< 0.2	< 0.2	0.30
221.35	68		0.40	0.35	< 0.2	0.45
	149	1.00	0.64	0.16		
221.5	27		0.50	0.30		0.30
	118	0.91	0.40	0.30	< 0.2	0.30
	148	0.90	0.69	0.14		
	150	1.00	0.55	0.15		
222.0	33	(0.6)	0.30	0.30		< 0.3
	34		0.40	0.35		0.40
223.0	45	(1.0)		0.20	< 0.2	0.30
223.07	136	1.08	0.67	0.24		
223.1	52	(0.9)	0.50		< 0.2	
224.5	66	1.05	0.30	0.20	< 0.2	0.55
231.0	40	(1.2)	1.00	0.25	< 0.2	
232.57	101	0.85	0.65	< 0.2	< 0.2	0.30
241.0	85	0.90	0.60	0.30	< 0.2	0.30
241.1	18	(0.8)	0.50	0.30		0.30
242.2	67	1.00	0.40	0.30	< 0.2	0.40

* Parenthetical values obtained at 0.01% Co.

(continued)

Table VI (Cont'd)

Type	No.	Results : γ .03 Co				
		Cobalt*	Manganese	Iron	Nickel	Lead
242.5	72	0.93	0.40	0.25	< 0.2	0.30
251.12	91	0.80	0.50	<0.2	< 0.2	0.25
251.2	1H		0.55	0.38	< 0.2	
	2H	(0.5)	0.67	0.27	< 0.2	
251.35	149	1.00	0.64	0.16		
251.5	118	0.91	0.40	0.30	<0.2	0.30
	139	0.75	0.69	0.21		
	148	0.90	0.69	0.14		
	150	1.00	0.55	0.15		
252.0	41	(0.9)	0.50		0.20	
252.2	67	1.00	0.40	0.30	< 0.2	0.40
252.25	4H	(1.0)		0.32	< 0.2	
252.5	69		0.30	<0.2	< 0.2	0.45
253.0	89	0.90	0.70	0.40	0.22	0.40
253.07	136	1.08	0.67	0.24		
253.1	52	(0.9)	0.50		< 0.2	
253.2	6H	(0.5)	0.72	0.28	< 0.2	
254.0	128	0.50	0.41	0.20		
254.5	66	1.05	0.30	0.20	<0.2	0.55
311.0	7	(1.3)				
	13	(1.3)	0.50	0.30		
	83	0.90	0.60	0.30	< 0.2	0.40
	88	0.90	0.60	0.35	<0.2	0.40
	104	1.05	0.55	0.30	<0.2	0.30
311.07	103	1.20	0.60	0.30	< 0.2	0.40
311.1	11	(1.1)	0.40			<0.3
	12	(1.5)				
	73	1.00	0.45	<0.2	<0.2	0.45
	102	1.00	0.60	<0.2	< 0.2	0.35
	105	0.88	0.50	0.30	< 0.2	0.35
	106	0.92	0.52	0.30	<0.2	0.35
	111	1.10	0.55	< 0.2	< 0.2	0.35
	112	1.13	0.55	<0.2	<0.2	0.35
	113	1.05	0.80	<0.2	< 0.2	
	116	0.88	0.35	0.20	<0.2	0.35
	117	0.94	0.40	<0.2	<0.2	0.30
	134	0.85	0.66	0.23		
	141	0.90	0.53	0.22		
312.0	152	0.42	1.36	0.43		0.26
312.1	76	0.87	0.95	0.30	<0.2	0.30
	77	0.92	0.95	0.35	0.24	0.35
	154					
312.17	107	0.58	1.40	0.46	0.23	0.35
312.27	M4		0.55	<0.2		
312.5	55					
	64	(0.2)	0.20		<0.2	0.25
313.0	M5		0.76		<0.2	
321.0	83	0.90	0.60	0.30	<0.2	0.40
	147	1.00	0.63	0.17		

* Parenthetical values obtained at 0.01% Co.

(continued)

Table VI (Cont'd)

Type	No.	Results : γ .03 Co				
		Cobalt*	Manganese	Iron	Nickel	Lead
321.1	73	1.00	0.45	<0.2	<0.2	0.45
	102	1.00	0.60	<0.2	<0.2	0.35
	105	0.88	0.50	0.30	<0.2	0.35
	106	0.92	0.52	0.30	<0.2	0.35
	143	0.92	0.48	<0.14		
322.0	32	(0.8)	0.50	0.30		<0.3
	153	1.65	0.59	0.38		0.44
322.1	76	0.87	0.95	0.30	<0.2	0.30
	77	0.92	0.95	0.35	0.24	0.35
	151	0.35	1.18	0.34		0.72
323.0	45	(1.0)		0.20	<0.2	0.30
331.0	14	(1.0)	0.50			
332.57	101	0.85	0.65	<0.2	<0.2	0.30
341.0	17	(0.9)	0.50	0.30		0.30
	19	(1.0)	0.50	0.35		0.30
	22					
	94	1.05	0.70	0.35	<0.2	0.40
	95	0.80	0.50	0.35	<0.2	0.45
	115	0.90	0.40	0.35	<0.2	0.30
341.07	96	0.96	0.70	0.30	<0.2	0.30
341.1	114	0.87	0.50	0.35	<0.2	<0.3
	138	0.90	0.53	0.24		
	143	0.92	0.48	<0.14		
341.5	70	0.60	0.95	<0.2	<0.2	0.20
	71	1.00	0.55	<0.2	<0.2	0.40
342.0	20	(1.0)	0.30			
	43	(0.6)	1.10	0.60	0.25	0.45
	47	(1.0)	0.50	0.20	0.30	0.65
	97	1.05	0.80	<0.2	0.23	0.35
	124	<0.20				
342.17	127	0.80	0.64	0.15		
342.5	72	0.93	0.40	0.25	<0.2	0.30
	11H	(1.0)		0.35	0.24	
343.0	21	(1.0)	0.70	0.30		0.30
	44	(0.8)			0.25	0.55
	M5		0.76	<0.2		
344.0	9	(1.0)	1.00	0.30		0.30
344.14	48	(1.1)				
344.34	42	(1.1)				
353.0	89	0.90	0.70	0.40	0.22	0.40
411.1	93	0.67	0.45	0.25	0.21	0.55
	75	1.17	0.65	0.35	<0.2	0.40
411.25	9H	(1.0)	0.68	<0.2	<0.2	
411.3	7H		0.77	0.45	0.23	
411.35	8H		0.59	<0.2	<0.2	
411.5	24	(1.0)				
	51	(1.0)	0.50		<0.2	0.30

---

* Parenthetical values obtained at 0.01% Co.

(continued)

Table VI (Concluded)

Type	No.	Results (γ .03 Co)				
		Cobalt	Manganese	Iron	Nickel	Lead
412.3	120				0.24	
	121	1.00	0.34		< 0.2	
	122	0.95	0.35		< 0.2	
421.12	5H	(1.0)	0.60	0.35	< 0.2	
441.3	7H		0.77	0.45	0.23	
441.35	8H		0.59	< 0.2	< 0.2	
511.0	39	(1.0)	0.40	0.30		0.30
511.2	119	0.64	0.25	< 0.2	< 0.2	
512.17	109	1.00	0.55	< 0.2	< 0.2	0.30
512.27	110	0.97	0.55	0.30	< 0.2	0.30
513.07	108	0.84	0.60	0.30	< 0.2	0.35
514.5	10H		0.66	0.32	< 0.2	
521.1	74	0.88	0.55	0.30	< 0.2	0.40
	90	0.45	0.65	0.30	< 0.2	0.55
522.0	32	(0.8)	0.50	0.30		< 0.3
542.5	11H	(1.0)		0.35	0.24	
543.0	44	(0.8)			0.25	0.55
553.2	6H	(0.5)	0.72	0.28	< 0.2	

Values in parentheses were obtained at concentrations of 0.01% cobalt.

In effect, these results* show:

1. Cobalt was unaccelerable beyond 20% by any amine. Those which showed some activity were 75, 112, 136, 97, 66, and perhaps 12.

2. Cobalt was retarded to the extent that drying rates less than 60% of the control were obtained by the following, again listed in order of decreasing potency: 124, 29, 64, 151, 31, 152, 90, 128, 2H, 6H, 28, 107, 43, 129, 16, 30, 33, 70;

3. Manganese was accelerated from 30% to 300% by numerous amines. The most influential compounds are listed in order of decreasing potency: 107, 152, 43, 40, 9, 78, 129, 151, 70, 76, 77, 132, 79, 113, 97, 7H, M5, 86, 6H, M3, 94, 96, 21, 87, 89, 148, G3, 130, 10H, G5, 75, 90, 98, 101, G6;

4. Manganese was retarded 20% to 50% by the following: 30, 64, G4, 119, 131, 20, 28, 31, 33, 63, 66, 69, 144, 126, 116;

5. Iron was accelerated from 50% to 400% by the following: 43, 107, 89, 19, 34, 37, 38, 68, 75, 77, 88, 94, 95, 114, 115, G1, G2, 5H, 11H, 7H, 1H;

---

* See Appendix II for names and classification.

6. None of the amines were able to accelerate nickel to a point at which it could be considered a drier. Finite drying times (γ = 0.2 to 0.3) were obtained with the following amines, while the uncomplexed metal was a non-drier: 47, 43, 44, 77, 120, 11H, 107, 7H, 97, 89, 93, 41;

7. Lead was accelerated to a maximum of 150% by the following: 151, 47, 53, 66, 44, 90, 93, 92, 46, 68, 69, 73, 95, 43, 71, 74, 67, 83, 88, 89, 75, 94, 82, 84, 86, 87.

Repeaters in the above group are listed categorically:

Table VII

AMINES EFFECTIVE WITH TWO OR MORE METALS

Amine	Cobalt		Manganese		Iron	Nickel	Lead
No.	Accel.	Ret.	Accel.	Ret.	Accel.	Accel.	Accel.
75	x		x		x		x
97	x		x			x	
28		x		x			
30		x		x			
31		x		x			
33		x		x			
64		x		x			
70		x	x				
151		x	x				x
6H		x	x				
152		x	x				
87			x				x
90		x	x				x
107		x	x		x	x	
43		x	x		x	x	x
89		x	x		x	x	x
93		x				x	x
77			x		x	x	
94			x		x		x
7H			x			x	
66				x			x
69				x			x
95					x		x
68					x		x
88					x		x

The behavior of a given additive often depended upon the age of the metal-catalyzed stock solution into which it was admitted. Because of this, many discordant results were obtained in the gathering of the data reported in this section, with the result that the comparisons given in the above tables are best viewed qualitatively. In all cases in which discrepancies exceeding 20% of the average value were observed a third determination was made using fresh stock. Generally, agreement with one of the two conflicting values was observed, in which case the problem of selecting the best average figure was resolved by using only the two concordant values.

Lest the reader gain the impression that data subject to such inaccuracies would better have been treated by statistical methods, the inadvisability of spending more effort on the screening operation for which the amine addition program was designed is pointed out at this time. Since any spectacular results were treated at greater length in more carefully controlled experiments, the possibility of a potent amine escaping detection is considered non-existent.

A summary of the screening studies of 150 amines can be made as follows:

Only five amines accelerated cobalt, none to an extent greater than 30% (γ = 1.3). Manganese was upgraded to an efficiency comparable to 0.03% cobalt by 44 amines, 24 of which imparted more than a 40% increase in the drying rate (γ = 0.70). Of the 24 top amines, 14 were tertiary, the remainder being distributed evenly among primary, secondary, quaternary, and miscellaneous. Of the 14 tertiaries, nine were heterocyclic.

The best manganese accelerator was a tertiary aliphatic amine (NN' disalicylalethylenediamine) whose structural characteristics cause it to resemble a tertiary heterocyclic amine on two counts: 1) the -N=C- linkage, and 2) the conjugation of -N=C with an aromatic system.

Iron catalysis was promoted by 59 amines, 20 of which imparted an efficiency approaching that of 0.03% cobalt ($\gamma = 0.35$). Ten were tertiary amines, of which six were heterocyclic, and an additional one was of induced heterocyclic character. Nickel was accelerated by 12 amines ($\gamma = 0.2$ to 0.3), but in no case was its activity brought up to a par with cobalt or manganese. Lead, which was accelerated by 41 amines ($\gamma = 0.35$ to 0.65), was employed in much higher concentrations than the other metals.

A comparison of the gamma values of the uncomplexed metal driers is given in Table VIII.

Table VIII

RELATIVE ACTIVITIES OF VARIOUS METAL CATALYSTS

Metal	Concentration	γ
Cobalt	0.03%	1.00
Manganese	0.05	0.50
Iron	0.05	0.20
Nickel	0.05	$\ll 0.20$
Lead	0.30	< 0.30
Rare Earths	0.06	0.22

The rare earths drier* included in Table VIII was evaluated with a selected group of 21 amines, with the findings that only four of the additives increased the drier activity of the catalyst. Only the Schiff's base (#107) had been found active with conventional metals. Results are listed below.

---

* Cerium and lanthanum naphthenates, provided by Advance Solvents Corporation.

Table IX

RARE EARTH STUDIES

Amine	Type	γ
19	341.0	0.30
38	122.0	0.27
71	341.5	0.27
107	312.17	0.27
40	231.0	0.23
65	122.0	0.23
70	341.5	0.23
96	341.07	0.23
47	342.0	0.23
93	411.1	0.22
13	311.0	0.21
18	241.1	0.21
94	341.0	0.21
12	311.1	0.18
64	312.5	< 0.19
78	131.0	< 0.19
85	241.0	< 0.18
74	521.1	$\ll 0.24$
17	341.0	< 0.05
30	221.1	< 0.05
9	344.0	< 0.05

Results of Detailed Studies

Subordinate only to the discovery that manganese is accelerable to a point at which it exceeds the activity of the cobalt standard is the finding that one of the most vigorous amines is inexpensive, readily available, easily synthesized and purified, and capable of wide variations in structure for purposes of developmental study. The amine in question is NN' disalicylalethylenediamine,

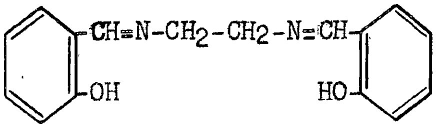


Figure 9. Schiff's Base

whose preparation (8) from ethylenediamine and salicylaldehyde proceeds smoothly to a yield considerably above 90%. This shall be referred to as Schiff's base with the realization that a wide variety of Schiff's bases is possible.

Acceptance of this amine by the industry requires that it find universal application in all types of vehicles as well as in pigmented systems. The latter issue has been taken up in Chapter 6; the former was subjected to the exhaustive tests described below.

Five purified oils and six raw linseed oil samples were charged with 0.10% manganese as naphthenate. Each was then subjected to a series of tests in which metal concentrations ranging from 0.01% to 0.06%, and amine-to-metal ratios from 0.04 to 0.4 (for the purified oils) and from 0.1 to 0.8 (for the raw oils) were employed. Results of drying tests made on the Gardner apparatus after aging times of 1 day, 1 week, and 1 month are given in Table X.

In each vehicle the initial activity of the complex far exceeded that of the uncomplexed metal; however, a truer picture of the spread of gamma values can be gained by comparison of the one-day-old samples, in which case the $\gamma_{0.05Mn}$ values ranged from 1.2 to 3.0. For clarity the results are expressed as percentage improvement over uncomplexed manganese, rather than as $\gamma_{0.05Mn}$. In passing, mention is made of the fact that the standard $\gamma_{0.03Co}$ values are almost exactly half of the $\gamma_{0.05Mn}$ values reported here.

An amount of amine much less than anticipated is sufficient to produce rapid drying. A ratio of 0.2 moles of amine per mole of metal is the optimum in most vehicles. Inferior oils are upgraded to a much greater extent than refined oils.

Table X

ACCELERATION OF MANGANESE CATALYSIS BY SCHIFF'S BASE

Oil	% Mn	Optimum Ratio	Maximum Percentage Acceleration			
			new	1 day	1 week	1 month
A-1	0.02	0.04	100	40	30	8
	0.04		100	20	20	0
	0.06		53	30	-	26
A-2	0.02	0.10	80	-10	16	7
	0.04		55	30	6	7
	0.06		70	50	22	7
A-3	0.02	0.04	-	180	51	13
	0.04		-	160	23	27
	0.06		-	140	20	41
A-4	0.02	0.10	230	200	55	31
	0.04		180	165	50	25
	0.06		140	120	110	15
A-5	0.02	0.10	-	180	50	20
	0.04		-	140	100	50
	0.06		-	150	130	85
B-1	0.02	0.20	200	170	180	-10
	0.04		220	120	-	20
	0.06		130	100	40	38
B-2	0.02	0.20	260	210	140	45
	0.04		160	130	80	68
	0.06		130	130	90	100
B-3	0.02	0.20	-	45	0	25
	0.04		-	140	80	60
	0.06		-	90	90	65
B-4	0.02	0.20	-	150	55	25
	0.04		-	150	25	25
	0.06		-	160	40	30
B-5	0.02	0.30	-	190	120	80
	0.04		-	100	75	50
	0.06		-	100	90	70
B-6	0.02	0.20	-	70	25	5
	0.04		-	80	30	10
	0.06		-	60	25	15

Legend for Table X:

A-1: Superb Linseed Oil
A-2: A. D. M. Alkali-refined Linseed Oil*
A-3: A. D. M. White Refined Linseed Oil
A-4: Sherwin-Williams Alkali-refined Linseed Oil
A-5: Sherwin-Williams Extracted Linseed Oil

B-1: A. D. M. ASTM Linseed Oil (Lehigh)
B-2: Sherwin-Williams Raw Linseed Oil
B-3: A. D. M. ASTM Linseed Oil (Advance)
B-4: A. D. M. ASTM Linseed Oil (Harshaw)
B-5: Spencer-Kellogg Expelled Linseed Oil
B-6: Sherwin-Williams Aged Raw Linseed Oil

More important than the effect of the vehicle was the finding that the Schiff's base complex reverted in time to a catalyst whose activity merely equaled that of the control (see Table X). From figures 10 to 21 (Appendix VI) the generality can be made that the maximum useful life of the additive is somewhat less than a month. Fortunately, the supercatalyst can be regenerated after at least six months' aging**, which implies that the Schiff's base complex had reverted irreversibly to a less active form, leaving behind uncomplexed manganese to react with the newly added Schiff's base.

In order to provide an article of commerce, a drier which will not change its activity on storage is a sine qua non. Consequently, the possible mechanisms through which the phenomenon referred to above can take place have been listed along with considerations for their solution:

1. Delayed salt formation.

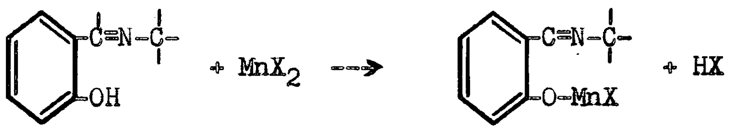
The phenolic group can react with the metal, in time forming a covalent bond which would enhance the tendency toward coordination.

---

* A. D. M. = Archer-Daniels-Midland Company.

** By this time all improvement in drying had been lost, and a tendency toward gammas below that of the control was detected.

The left half of the amine molecule is used for illustration:



The effect of the formation of two chelate rings from a repetition of the above process involving the other half of the Schiff's base is believed to be deleterious. However, the reasons for this belief must be withheld until Chapter 7.

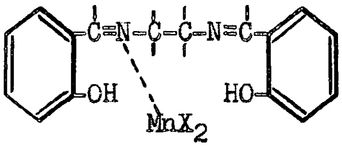
This phenomenon of delayed salt formation can be side-stepped by the use of benzaldehyde instead of salicylaldehyde. Work currently in progress indicates that the original activity of the Schiff's base made from benzaldehyde is less than that of the one bearing the phenolic group, however.

2. Disproportionation.

The particular ammine species to which the unusual reactivity of the Schiff's base is attributed may disproportionate into more highly coordinated and correspondingly less highly coordinated species, both of which may be less active than the original:

$$2Mn(A)X_2 \longrightarrow MnX_2 + Mn(A)_2X_2$$

In the case at hand, the active species is believed to be the half-coordinated monoammine:



which, in time, either a) picks up another amine, or b) loses the amine to another manganese ion. A tendency toward coordinating with the second nitrogen is believed to be held in check by resonance of the structure. In the case of delayed salt formation, the establishment of the chelate ring would be the driving force for multiple coordination.

If disproportionation is the cause of the difficulty encountered in the use of Schiff's base, the answer will be found only in a tailor-made molecule containing perhaps only one nitrogen group. Again, a thorough discussion of the possibilities requires a knowledge of the theoretical aspects which appear later in the report.

At the time of complex formation the statistical distribution of amine groups among the manganese ions probably occurred. Such a system would contain all species of the imperfect* complex in equilibrium so long as the valence of manganese remained unchanged. If one of the species possessed an exceptionally stable configuration, then perfection of the complex would result. In the case of cobalt this would be accompanied by irreversible oxidation of the metal.

3. Changes in structure.

If the manganese complex reverts to a less active form owing to a change in structure, then the change may be retarded or stopped by an increase in the rigidity of the organic skeleton. Calvin has shown that the cobalt complex exists in three different solid forms, only one of which is capable of absorbing oxygen reversibly; solutions of the manganese salt may suffer the same malady. Whether the structure

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* An imperfect complex is characterized by the equilibration among the various species. Perfect complexes are much rarer, but one such series is the cobalt (III) hexammines.

change is initiated by oxidation, by hydrolysis, by heat, or by other means, is not known; however, some chemical reaction is necessary to effect the change (115).

The solution to this problem will be found in increasing the rigidity of the amine portion of the molecule, for the singly bound pair of carbon atoms of the Schiff's base made from ethylenediamine is blamed for the wide variety of stereochemical patterns into which the complex fits. The use of ortho phenylenediamine in place of ethylenediamine will shore up the limber part of the molecule, but at the same time would increase the inductive displacement of electrons away from the nitrogen atoms.

In passing, mention is made of the fact that a change in structure cannot occur without a concomitant change in the bond function. Fernelius* has pointed out (56) that an ion which normally assumes a planar configuration can be forced to adopt some other form by the use of a chelating group incapable of assuming the planar structure. This, of course, involves different orbitals from the dsp^2 configuration sought by the metal ion.

Economics of Amine Addition

As a competitor with cobalt on a cost basis, alone, the Schiff's base complex of manganese shows promise so long as the molar ratio of amine to metal can be kept below 0.2, as shown in Appendix VII. As a drier stabilizer, even in pigmented systems it offers many advantages.

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* See also References 57, 115, 122 and 124.

Real economies are anticipated when the technology of complexed iron catalysts has advanced as far as the manganese - Schiff's base complex. The success of the complexing program has been assured more by the special effects of complex catalysis and by the realization that cobalt can be replaced by a less critical metal than by economic considerations alone.

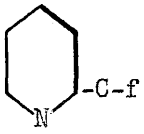
The present status of the program is that an additive has been found which enables manganese to surpass cobalt as a drier, and which elevates iron to a point where it is a serious contender for consideration as a primary drier. While a catalyst which can be used by the varnish formulator has not yet been developed owing to deterioration during storage, indications exist that further developmental work will overcome that obstacle.

Interpretation of Results

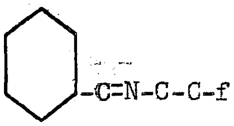
In most cases an additive which was found to be effective with manganese, iron, and nickel possessed a resonant structure which had two opposing effects:

1. The basicity of the amine was reduced;
2. The coordinating tendency of the amine was restored partially by structural effects to compensate for the reduced basicity.

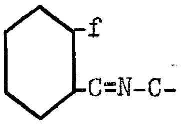
This structure is found in the central groupings,



Type I: Heterocyclic



Type II: Side-chain Schiff

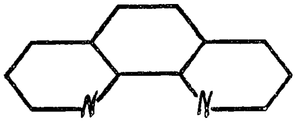


Type III: Ortho Schiff

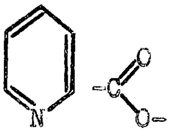
Here, f is an electron-donating functional group. Note that five- and six membered rings result from chelation in each case.

The doubly bound, resonating nitrogen appears to be the keystone in the construction of the chelate. Clearly, two conditions must be satisfied in order for an amine to be active with manganese: the nitrogen must be conjugated with, or part of, an aromatic ring, and a chelate involving five or six elements (including the metal) must be possible. Experimental observations leading to this view have been cited earlier. A more detailed discussion follows.

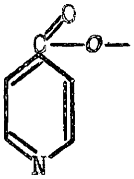
Orthophenanthroline, the most outstanding amine, fits into the first category:



(the second nitrogen plays the role of the functional group). Picolinic acid, also falls into this class; for here the functional character is supplied by the carboxyl group. This amine is active.



while isonicotinic acid, its vinylog, is not active.*



Nicotinic acid, not a vinylog, is not active.*

The second and third types start with the skeletal structure of N methyl benzalimine,

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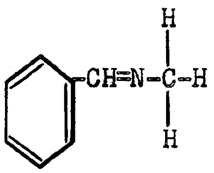
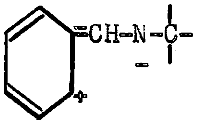
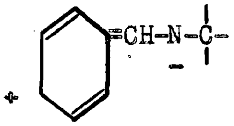
*Isonicotinic acid satisfies the electronic requirements for resonance, but would require a 7-membered ring. Nicotinic acid is "out of step" electronically.



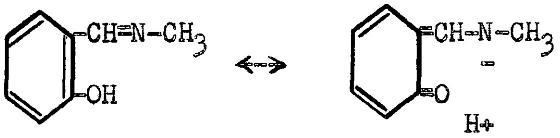
whose resonance extremes, if they existed, would be

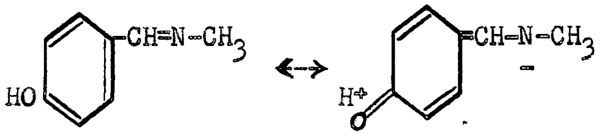


and



Owing to the necessity of destroying the aromatic character, the balance is too far in favor of the unpolarized form to permit much resonance contribution; however, if a group is put into the ortho or para position which will induce the formation of the positive charge, the result should be a resonant benzalimine; e.g.

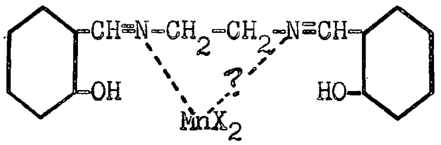




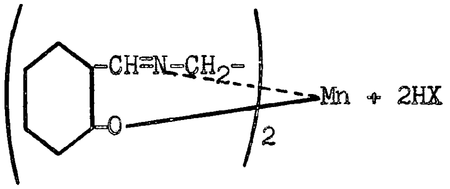
Note, further, that these forms satisfy the resonance requirements that the number of unpaired electrons be identical in both extremes.

Reaction of the ortho-substituted compound with the metal would give rise to a chelate, producing the pseudo heterocyclic character alluded to earlier.

NN' disalicylalethylenediamine fits into both of the last two categories listed at the beginning of this section. The two nitrogens produce a bidentate amine which may or may not coordinate through both nitrogens simultaneously,



but the presence of both hydroxyls may lead to



in which both nitrogens are believed to be coordinated.

Until this happens, however, the hydroxyl groups may function merely as centers for coordination. If they do, the chelate is believed to be a hybrid of the resonance forms:*

Aliphatic diamines exert a retarding effect on both cobalt and manganese. Because these amines are strongly basic the belief is held that two coordination positions are filled by one amine; and because of the possibility of chelation, one can assume that one metal atom supplies both of these coordination positions. If the metal is cobalt, the configuration is that represented by the diammine species of Table II (q.v.); if the metal is manganese, the configuration resembles the monoammine of Table II. The possibilities are compared with the configuration of uncomplexed cobalt in Table XI, below:

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* Plus two more from participation of the right hand side of the molecule. The necessity for considering partial chelation is brought out in Chapter 7 where an electronic hypothesis is advanced. The experimental data will fit best if this view is accepted.

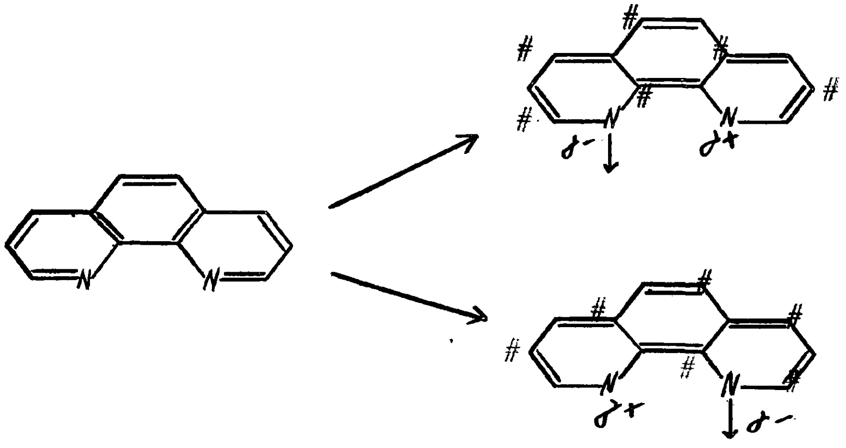
Table XI

ELECTRONIC CONFIGURATIONS OF DIAMMINES

	3d					4s	4p	
CoX_2	••	••	•	•	•	•o	•o	
$Co(A)_2X_2$ *	••	••	••	xx	xx	•o	•o	•
$Mn(A)_2X_2$ *	••	••	xx	xx	•	•o	•o	

Note that in the complexes only one half-filled orbital is present, while in uncomplexed cobalt three such orbitals are present. The significance of this observation will be pointed out in Chapter 7.

With the heterocyclic diamines the situation is different,** provided one is willing to relinquish the orthodox view of chelation in favor of the proposal that only one nitrogen at a time coordinates with the central metal. Application of the resonance concept leads to the polarized structures for orthophenanthroline: (actually, the carbons labeled # carry the positive charge)



in which the supposed resonance exists between the two forms on the right, not between the polarized and non-polarized forms. Since all five of the 3d orbitals of manganese are of equal potential, no

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* In this case $(A)_2$ is represented by one ethylenediamine.

** We know their behavior is different; as a consequence we postulate a difference in the electronic structure of the complex.

difficulty is encountered in accommodating the two different pairs of electrons in different orbitals and at the same time meeting the resonance requirement that the two forms possess the same energy. The net result is an electronic configuration resembling a monoammine in a structure possessing the steric and structural features of the more favored diammine.

Bailar has noted that strongly basic or negative groups stabilize the higher valence states of a complexed ion (43), but that large groups with resonating structures stabilize the lower valence states. This empirical result is in accord with the observations made above, and with Werner's original observation in 1912 (166) that the ferrous dipyridyl complex was stable.

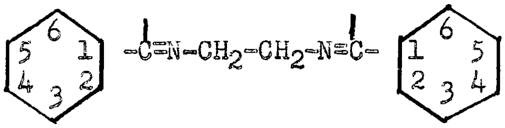
Future Work on Amine Addition

Outside of the fact that hundreds of amines remain on the list of untried additives, and could be added to the list if labor were available to carry on the preliminary screening, only those amines which fit into classes 312, 341, and perhaps 142, 221, and 251 should be considered seriously. Cobalt offers no promise of being accelerable by any amine.

In the event the amine additive program were to be reopened, the suggestion is made that the amine ratio be 1:1 or less, and that all tests be run at the same percentage metal (0.03% would suffice). Films should be spread after the complex sample had aged one day, and again after one month.

Specially prepared amines which would be studied comprise four groups as follows:

1. Nuclear substituted Schiff's bases:



Substituted at Carbons #2, by -OH
$-OCH_3$
-COOH
-Cl

Substituted at Carbons #3 and #4, in turn, by the same groups.

2. Substituted in the Amine Fragment by a) propylenediamine, b) acetylenediamine, c) benzidine, d) m phenylenediamine, and e) p phenylenediamine.

3. Monodentate Schiff's bases prepared by reaction of salicylaldehyde and benzaldehyde with selected primary amines.

4. Tridentate Schiff's bases prepared from triamines.

Many more benefits are expected to accrue from a continuation of the studies described in the next two chapters, in which complexes will be constructed along the lines prescribed by theory using materials dictated by the purse. As a screening operation for new candidates, amine addition is valuable in that the metal concentration can be controlled and the amine ratio varied at will; for these reasons, and also because the operation is simple, an amine addition program will accompany any research on complexes done in this laboratory.

CHAPTER 5

COMPLEX PREPARATION AND EVALUATION

Purpose of the Study

As a supplement to the amine addition program, preformed complexes of cobalt, manganese, iron and nickel were prepared for evaluation as varnish and ink driers. Under these conditions no doubt existed as to whether a complex actually had formed.

Unlike the additive program, the all-important metal concentration could not be relied upon to be constant throughout all of the tests. Furthermore, many complexes, particularly those of the amino acids, were sparingly soluble in linseed oil; and since their solubilization required the use of a mutual solvent, a new variable resulted. Despite the inaccuracies arising from the necessity of assuming a metal content based on theoretical values, the complexing method of testing many of the promising amines was useful with iron and nickel, whose uncomplexed activity was practically non-existent. Even with manganese, some quantitative evidence of activity was possible in cases in which the complex was isolated in the solid state.

Methods of Preparation*

1. Calvin's Complexes.

The important series of salts made from NN'disalicylalethylenediamine was prepared according to the method published in Inorganic Syntheses (8), in which a boiling aqueous solution of the amine was

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* See References 85, 112, 113c, 114, 127, 129, 166, 167, 168, 175, 176.

added to a solution of the metal salt. The purified complex was dissolved in linseed oil to make a varnish containing 0.05% metal (0.03% in the case of cobalt).

2. Chelated Salts.

Salts of the alpha amino acids were prepared by addition of an aqueous solution of the metal ion to a solution of the amino acid to which had been added sufficient alkali to dissolve the acid. Crystalline products were obtained in every case, and most were purified out of ethanol before testing.

Ferric tyrosinate, N phenyl glycinate, and albuminate were made in soluble form by preparing the salt in molten ferric chloride hexahydrate and dissolving the resulting solution in linseed oil. One beta amino acid salt was prepared by this method.

3. Simple Coordination Compounds.

One particularly interesting preparation, the results of which are discussed in Chapter 6, involved an amine bicarbonate and the metal chloride as starting materials. Presumably, the reaction was

$$nRNH_3.HCO_3 + MeCl_2 \longrightarrow Me(RNH_2)_nCl_2 + nH_2O + nCO_2,$$

in which the acidic character of the metal salt decreased with each successive acquisition of amine, perhaps to the point at which further addition was prevented by the bicarbonate group. An acid stronger than carbonic would be required to complete the reaction.

Orthophenanthroline was complexed with metals in a variety of ways, the most favorable of which involved precipitation of the complex* out of ethanol solutions of the metal salt and of the amine. When heated, the complex dissolved permanently in ethanol.

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* A single species can be isolated, in contrast to the equilibrium which exists in solution. This is discussed later.

In many cases the amine served as the solvent. Especially adaptable to this method was pyridine, in which all of the metal salts were soluble. In general, the complex could be isolated in the solid state by dilution of the pyridine solution with ether.

A series of experiments requiring the use of esters of amino acids* led to the discovery of an unusual preparation of an unusual drier: esterification of glutamic acid via reaction with butyl alcohol in the presence of sulfuric acid and addition of the ester to molten ferric chloride hydrate produced a catalyst which possessed peculiar properties when made according to the following specifications:

> To 0.77 g. glutamic acid in 6.0 ml. n butanol is added 0.3 ml. conc. H_2SO_4. After refluxing two minutes, 0.81 g. $FeCl_3.6H_2O$ is added and the mixture again refluxed. Heating is increased until sufficient butanol is removed to permit a sudden darkening of the mass, whereupon 5.0 ml. of linseed oil is added.

The proper technique for preparing the catalyst is to remove much of the excess butanol until the point is reached where incipient decomposition is detected by a sudden deepening of color. Excessive heating produces an insoluble gel; insufficient heating results in an inactive compound. An excess of sulfuric acid over that required to catalyze the esterification of the amino acid is used. That this may result in ring closure of the glutamate has been postulated, and is discussed in the next section under iron complexes.

The best general method for the preparation of complexes, especially when a series containing varying amine ratios was desired, was to reflux a mixture of toluene, the amine, and a metal salt until solubilization resulted. This method has been employed successfully in

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* These differ from the metal salts in that chelation is not likely.

the preparation of amylamine and pyridine complexes of cobalt and manganese. By careful weighing of the metal salt, a solution was obtained which could be diluted with linseed oil to the desired metal concentration.

In some cases a preliminary refluxing of the metal salt was employed to remove water of coordination, thus enabling the use of commercially available salts.

Results of Complex Evaluation

1. Cobalt Complexes.

Fifteen cobalt complexes were prepared, analyzed, and evaluated as driers where possible*. Initial results indicated that the activities of virtually all of the complexes slightly exceeded that of the uncomplexed metal when tested at a concentration of 0.01% cobalt, but that the superiority of the complexes disappeared at the standard 0.03% concentration.

Table XII lists the complexes of cobalt which had been made up to the time the emphasis shifted to iron and manganese. Two types of complexes were recognized: 1) the additive type, in which amine groups coordinated with the cation of cobalt acetate; and 2) the replacement type, in which the anion was replaced by a covalently attached chelating group.

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* Insolubility prevented the testing of several of the preparations at a known concentration; others were made in quantities too small for evaluation; inaccuracies in the analytical method, which was not designed for complexes, detracted from the results of the remainder.

Table XII

COBALT COMPLEXES

Compound	% Cobalt		Color	Solubility
	Act.	Theor.		
Additive Type				
Dicyclohexylamine	34.3	11.5	Bluish	——
Dicyclohexylamine	—	11.5	Violet	Isopropanol
Ammonia	—	—	Violet	Isopropanol
Pyridine	20.1	17.6	Rose	Isopropanol
Pyridine	20.6	17.6	Violet	Isopropanol
Pyridine	18.8	17.6	Rose-brn.	Isopropanol
Vinylpyridine	2.4	15.2	Violet	Isopropanol
Lutidine	29.7	15.2	Violet	Isopropanol
Quinaldine	25.0	12.7	Violet	Hot i propanol
Cyclohexylamine	—	—	Violet	Toluene
Replacement Type				
α nitroso β naphthol	—	14.7	Maroon	——
Glycinate	16.8	21.0	Violet	——
N phenyl glycinate	14.0	16.5	Rose	Linseed oil
Isonicotinate	16.9	19.5	Rose	——
Tyrosinate	33.5	14.0	Blue-gray	——

2. Manganese Complexes.

When manganese acetate was refluxed with a toluene solution of cyclohexylamine, a brownish red solution resulted. Because solubility was not complete, quantitative evaluation was not possible; however, linseed oil films prepared using the toluene solution were rapid driers.

The encouraging result obtained with this one manganese complex was forced into the background by the phenomenal results encountered with iron. The preparation and evaluation of manganese complexes will have been facilitated by the techniques developed with cobalt and iron, in the event further study along these lines is contemplated.

3. Iron Complexes.

Partially because of the special effects described in the next chapter, but chiefly because it offered a fertile field* for investigation, iron was employed most extensively of all the metals in the preparation and evaluation of complexes. In effect, the work was divided into two categories: 1) homogeneous catalysts, and 2) emulsion catalysts. All work was performed using ferric iron unless otherwise specified.

In the first group, the most headway was made in the amino acid series, where several active iron catalysts were uncovered. Reaction of aqueous $FeCl_3$ with various amino acids was instantaneous, even in cases in which the amino acid was only sparingly soluble in water. The complexes were water-soluble and imparted a deep red coloration to the solvent, but were insoluble in all of the organic media tried, including linseed oil.

Complexes made by the addition of an amino acid to molten $FeCl_3.6H_2O$ exhibited the same solubility characteristics. Dilution with water produced blood-red solutions, while organic solvents were ineffective.

A different aspect was placed on the work when an N-substituted amino acid was used. Ferric N-phenyl glycinate, produced by mixing dilute solutions of the potassium salt and ferric chloride, was water-insoluble, but dissolved readily in acetone. Analysis of the product obtained by evaporating the acetone solution was correct for $(C_8H_8O_2N)_3$ Fe, but the air-dried product no longer dissolved in organic solvents. When it was gotten into linseed oil by strong heating, the resultant dark-colored varnish was a drier**.

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* From the standpoints of expense, solubility of the starting materials, and theoretical interest, iron is the most promising candidate for long range complexing studies.

** A solution containing 0.04% Fe was the equivalent of 0.016% Co.

Two other preparations of ferric N-phenyl glycinate, made in strongly acidic solutions to avoid the possibility of $Fe(OH)_3$ formation, possessed the same drying characteristics as the first preparation.

Ferric citrate and ferric tartrate were subjected to a number of solubility tests with the result that no organic solvent was found. In an effort to produce an oil-soluble product, and at the same time perhaps a colorless one*, ferric citrate was dissolved in 85% phosphoric acid and diluted with linseed oil to a solution containing 0.04% iron. Both objectives were attained, but not simultaneously: the colorless phosphoric acid solution produced the typical dark coloration of organically complexed iron on dissolving in linseed oil. Moreover, the mixture was not a drier.

The statement was made earlier that the ferric salts of the amino acids were oil-insoluble. In order to prepare a salt of considerable solubility in linseed oil, glutamic acid** was treated with butanol in the presence of H_2SO_4 in the hopes that the monoester could be produced. On addition of $FeCl_3$ a catalyst was obtained which was either a drier or a non-drier, depending on the method of preparation (q.v.).

The structure of the catalyst was determined by Dr. Emory Parker of the Advance Solvents Corporation to be a pyrrolidone:

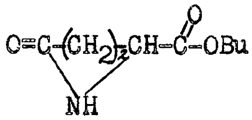

Figure 22. Active Pyrrolidone Complexing Agent

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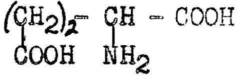
* Iron phosphate complexes are characterized by their lack of color.
** A dibasic acid of the structure



$\underset{\mathrm{COOH}}{(CH_2)_2}-\underset{\mathrm{NH_2}}{CH}-COOH$

In order to produce the half ester, a lower reaction temperature would have to be employed, as the ring closure (39) occurs above 120°C.

Chief interest in this compound centers around the special effects which resulted from its use, and which are discussed in the next chapter.

Considerably more difficulty was encountered in the preparation of oil-soluble addition* complexes of iron than when the central metal was cobalt. Moreover, the iron complexes tended to be highly colored. For these reasons, the results listed below for soluble iron complexes are representative neither of the effort put into their preparation, of the amount of work remaining to be done in developing them further, nor of the anticipated benefits which will accrue to further study of this interesting class of compounds.

Prepared complexes which have been demonstrated successfully as driers are listed below:

Table XIII

CATALYTICALLY ACTIVE IRON COMPLEXES

Ferric Complex	Remarks
Tyrosinate	Tack-free in 40 hours.
Pyrrolidone complex	Tack-free in 40 hours.
N phenyl glycinate	Activity equaled 0.01% Co.
Aminoguanadine oleate	Tack-free in 40 hours.
Albuminate + $FeCl_3$	Tack-free in 40 hours.

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* As opposed to the replacement type discussed earlier.

Other iron complexes showed less promise as driers. They are listed below:

Table XIV

INACTIVE IRON COMPLEXES

$FeCl_3$ + orthophenanthroline in ethanol.
N alkyl beta amino propionate.
$FeCl_3$ + pyridine in excess.
$FeCl_3$ + salicyladoxime.
Ferric citrate.
Ferric tartrate.
Ferric phosphate.
Ferrous phosphate.
Ferric aminoguanadine chloride.

4. Nickel Complexes.

As in the building of manganese complexes, only one method of preparation was employed with nickel. Repetition of the toluene process in which nickel chloride was employed as the metallic ingredient, did not follow the same smooth course of reaction observed with cobalt. Refluxing with amine had no apparent consequence at first; then the solid $NiCl_2$ began to swell into a greenish white mass which disintegrated on shaking. This product was virtually insoluble in acetone and water (as well as in toluene) but dissolved in pyridine and butanol. A linseed oil solution of these did not dry.

5. Calvin's Complexes.

The complex, bis (disalicylalethylenediamine) μ-aquo dicobalt (II) and similar complexes of iron, nickel, manganese, and chromium were prepared according to the directions given in Reference 8. Considerable difficulty was encountered in solubilizing several of the complexes in linseed oil, but eventually all were tested as driers. Of the five derivatives, manganese alone was active. This is in agreement with the amine additive results reported earlier.

CHAPTER 6

SPECIAL APPLICATIONS OF COMPLEX CATALYSTS

Alkali-Resistance of Varnishes

In conjunction with the evaluation of films in the Gardner apparatus, the glass slides were cleaned in a caustic bath after each use. On January 9, 1951 the startling observation was made* that one of the films emerged from the alkali bath with only a partial softening, rather than having suffered complete removal.

Because of the distinctive characteristics of the film, no difficulty was encountered in tracing the complex which had been responsible for the unusual effect described above, nor in reproducing it with the sample on hand. The catalyst was the ferric salt of the _sic_ partially esterified glutamic acid whose preparation has been described earlier.

That the unusual properties, as well as the drier activity, were attributable to the formation of the supposed pyrrolidone structure was evident from the fact that the glutamic ester was unique in its ability to impart alkali-resistance to a varnish film. Ferric salts of the amino acids performed no such feats. Later developments showed that another amine imparted alkali-resistance to certain pigmented systems, ** but that it was not even a drier in varnishes.

Iron Emulsion Catalysts

In order to evaluate several promising candidates among the

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* See Record of Original Data.
**See page 72.

complex iron catalysts, the expedient of emulsifying the aqueous complex with linseed oil was adopted. Precedence for the use of this technique had been established by Robinson (132) in her original work on the oxygen uptake of linseed oil-hemin emulsions.

One particularly interesting amine was aminoguanadine bicarbonate. Because it exemplifies one of the smoothest methods of preparation available for stepwise filling of coordination positions in the metal*, it was examined at length in the form of its aqueous complex with iron. Results given in the following table show that at least a 2:1 molar excess of iron is necessary** for effective catalysis.

Table XV

IRON AMINOGUANADINE CHLORIDE CATALYST EVALUATION

Moles Fe/moles amine	1/3	1/2	1	1-1/2	2
Tack-free time (hrs.)	30++	30++	30+	30	24

None of the films possessed alkali resistance, as did the film containing the pyrrolidone complex of iron. The aminoguanadine catalyst is most useful in certain pigmented systems, as will be shown later.

When the data on emulsion catalysts were reported at the Third Technical Conference on March 1, 1951 the decision was made to abandon any line of attack which would result in the inclusion of water in oleoresinous vehicles. Objections to the use of emulsion catalysts stemmed from:

1. The psychological effect on the consumer,

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* The metal competes with bicarbonate; the amine competes with water.
** See Record of Original Data.

2. Production difficulties,
3. The possibility of freezing, and
4. Improper functioning of the product (e.g., bleeding in lithography).

Loss of Drying in Inks

The first complex to be tested as an ink drier was dipyridino cobalt (II) acetate. A yellow lake pigment was milled with an equal weight of linseed oil containing 0.3% cobalt as the naphthenate; a similar formulation contained an equal quantity of cobalt in the form of $Co(py)_2(OAc)_2$. Initial drying times (paper offset) were recorded, after which the inks were aged for periods of five days, 47 days, and eight months. Results appear below:

Table XVI

COBALT COMPLEXES AS INK DRIERS

Catalyst	Paper Offset Times (hours)			
	Fresh	5 Days	47 Days	8 Months*
Control	6.1	15	26	>24
Complex	7.3	5	24	15

* Drying temperature 90°F.; others were 80°F.

Later, when the Schiff's base was developed as a varnish drier, two series of inks were made using the manganese complex of NN'disalicylalethylenediamine as the catalyst, with TiO_2 pigment in one series and yellow lake in another. The drying times of the complex formulations were compared with those of controls made using a conventional manganese catalyst of the same concentration; consequently, gamma values are based on the manganese control in this case.

Table XVII

PAPER OFFSET TIMES OF SCHIFF'S BASE-CATALYZED INKS

Pigment	Catalyst	γ New	γ 6 mos.
TiO_2	0.2% Mn	1.0	1.0
	0.2% Mn + 0.02% amine	1.2	1.3
Yellow lake	0.6% Mn	1.0	1.0
	0.6% Mn + 0.02% amine	1.7	0.9

Obviously, the Schiff's base complex is more susceptible to loss of drying power on aging than is the conventional drier. The drying loss phenomenon has been attributed to adsorption (176) and deactivating by-products (113b), but the question does not have a universal answer.

Alkali-Resistant Inks

Iron aminoguanadine chloride was tested in a yellow lake ink for the purpose of combatting loss of drying on aging. Despite the fact that the initial drying of the ink was retarded by the addition of 0.15% Fe to 0.15% cobalt, the dried ink was impervious to alkali, while the control was removed completely from the glass test slide in the same alkali bath. This discovery was made* and witnessed on January 30, 1951, and was followed by an extension of the work to a series of inks made from different pigments. Sixteen cobalt-catalyzed formulations** were made, half of which contained iron as the aminoguanadine complex in aqueous solution. The pigments used are listed in Table XVIII.

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* See Record of Original Data.

** Catalyst: 0.15% Co + 0.15% Fe (as chloride) for even-numbered controls; as complex for odd-numbered inks.

Table XVIII

IRON-AMINOGUANADINE INKS

Specimen #	Pigment	Control #
1	40% Ba lithol toner	2
3	45% Persian orange	4
5	50% Multifex	6
7	50% Hydrite	8
9	65% TiO_2	10
11	50% Milori blue	12
13	25% Peerless black	14
15	50% Yellow Lake	16

Results of drying tests, alkali resistance studies*, and behavior on aging are given in Table XIX.

Table XIX

AGING RESULTS, OFFSET TIMES, AND ALKALI RESISTANCE OF VARIOUS INKS

	Initial Results		Aged One Month	
Ink #	Offset Time (hrs.)	Alk. Res.	Offset Time (hrs.)	% Loss on Aging
1	6.2		7.0	13
2	2.4		4.4	83
3	7.9		11.6	47
4	5.6		22.0	294
5	2.0		3.0	50
6	1.4		2.6	86
7	2.4		4.1	71
8	1.6		3.6	125
9	3.3		3.6	9
10	1.5		2.3	53
11	10.0	x	7.7	-23
12	6.2		11.2	80
13	>20		>20	--
14	>20		>20	--
15	4.3	x	13.4	210
16	6.2		12.6	103

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* See Table XVIII. Even-numbered inks are controls.

The disappearance of alkali-resistance on aging was a discouraging feature of the study reported above, until the additional circumstance was noted that a yellow lake ink film which had survived the attack of alkali in the first tests on unaged inks was alkali-resistant even after six months. Apparently the caustic treatment "fixed" the film in the resistant condition in which it originally existed.

That the aminoguanadine complex is unique among all of the catalysts in its ability to impart alkali-resistance at least to yellow lake inks has been demonstrated by a second series in which the nature of the iron catalyst was varied. Six formulations were made early in 1951 (Table XX), and tested for offset time on glass (Table XXI), dry time on paper (Table XXII), and color of print (Table XXII). These were tested after six months' aging* for offset time on glass (Table XXI). In addition, the alkali-resistance of the formulations was noted.

Table XX

IRON-CATALYZED INKS

#	Metal Content
1	0.15% Co.
2	0.15% Co, 0.15% Fe as aq. aminoguanadine complex.
3	0.15% Co, 0.15% Fe as albuminate.
4	0.15% Co, 0.15% Fe as aq. $FeCl_3$.
5	0.075% Co, 0.15% Fe as aq. aminoguanadine complex.
6	0.075% Co, 0.30% Fe as aq. aminoguanadine complex.

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* In this case the ink, not the dried film, was aged.

Table XXI

OFFSET TIMES AND ALKALI-RESISTANCE OF IRON-CATALYZED INKS

	Initial Results		Aged 6 Months	
Ink #	Offset Time (hrs.)	Alk. Res.	Offset Time (hrs.)	Alk. Res.
1	6.5		>21	
2	8.3		8.0	
3	6.2		13.5	
4	9.2		14.5	partly
5	12.0	partly	15.5	yes
6	16.0	yes	11.5	yes

Table XXII

PAPER DRY TIMES OF IRON-CATALYZED INKS

Ink #	Cumberland Coated	Energy Bond	Color Sequence
1	10 min.	40 min.	3
2	10	280	5
3	10	10	1 (lightest)
4	10	180	2
5	10	240	4
6	10	150	6 (darkest)

When this information is added to the fact that dried yellow lake films lose their alkali resistance on standing one month, the role of the iron catalyst can be seen to be quite complex. The above tables reveal that the aminoguanadine complex not only minimizes loss of drying on aging, but is more likely to produce an alkali-resistant film on storage than before.

Figure 23 is an actual photograph of a group of alkali-resistant inks and their companion controls. Four of the films contained a yellow lake pigment; and two, a Milori blue pigment. All had been immersed partially in alkali for one-half hour two days after the films

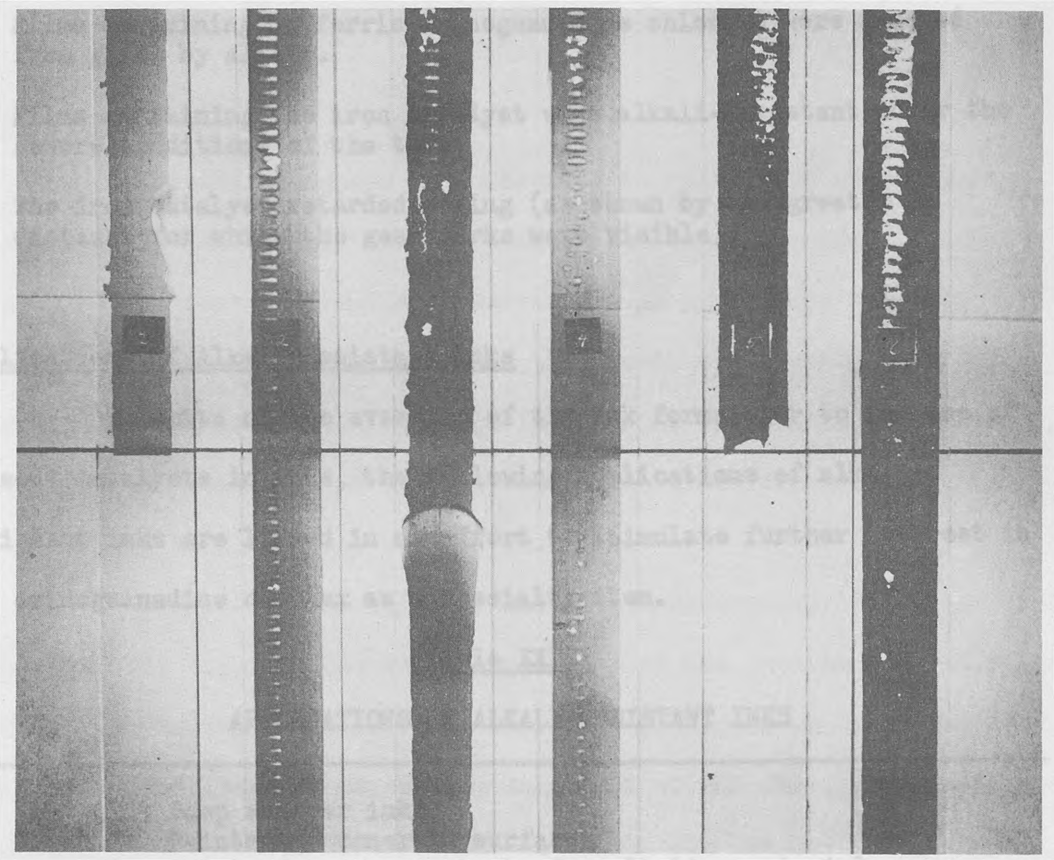

Figure 23

Alkali-Resistant Inks

Conditions: Films 1-4 immersed 1/2 hour to height denoted by dark line in 10% NaOH at 32°C. two days after hardening. Films 5-6 treated similarly with 5% NaOH at 40°C. Films were .001" thick.

Description of Films:

1. 0.15% Co in B and S yellow lake ink #76219A.
2. 0.075% Co, 0.15% Fe (aq.) in same.
3. 0.15% Co, 0.15% Fe (aq.) " "
4. 0.075% Co, 0.30% Fe (aq.) " "
5. 50% Milori Blue in 23p. trans. litho. varnish; 0.15% Co.
6. Same plus 0.15% Fe (aq.).

(all percentages based on total ink)

R.M.
4/7/52

had dried. From the legend beneath the photograph of the films, the following observations can be verified:

1. Films containing no ferric aminoguanadine chloride were removed from glass by alkali.
2. Films containing the iron catalyst were alkali-resistant under the severe conditions of the test.
3. The iron catalyst retarded drying (as shown by the greater distance for which the gear marks were visible).

Applications of Alkali-Resistant Inks

In spite of the aversion of the ink formulator to the use of aqueous catalysts in inks, the following applications of alkali-resistant inks are listed in an effort to stimulate further interest in the aminoguanadine complex as a specialty item.

Table XXIII

APPLICATIONS OF ALKALI-RESISTANT INKS

1. Soap wrapper inks
2. Paints for concrete surfaces
3. Paints for storage tanks for alkaline materials
4. Paints for washable surfaces

Future Work on Complexes

In addition to plans for undertaking a major exploration on iron and manganese complexes based on the findings of Chapter 4, metal salts of various amino acids will be synthesized. In short, addition complexes will be prepared using amines possessing no acid group; and replacement complexes will be synthesized from amines containing a carboxyl or other acid group.

CHAPTER 7

AN ELECTRONIC EXPLANATION OF CATALYSIS

The Development

Several phenomena were observed to occur with striking regularity in the amine addition and complex evaluation program. On the basis of the most outstanding observations an hypothesis has been advanced to explain the role of the electronic configurations of the metal ion in question. A means of testing the hypothesis was devised*, but owing to difficulties encountered in using the currently available equipment a complete test was not possible.

Despite the novelty of some of the assumptions and suggestions made in this chapter, the belief is held that the path is cleared toward the development of an electronic theory of catalysis which can be used in future complexing studies. Because most of the assumptions made here already have received wide acceptance (140); and because the present contribution has been essentially a coalescence of the thoughts of workers in the fields of atomic structure, complex formation, and the mechanism of autoxidation, the hypothesis as it presently stands is deemed worthy of serious consideration.

Until wider acceptance of the proposals submitted here has been gained, the explanation of catalysis cannot assume the stature of a theory. The research program which has been initiated in order to test the hypothesis has been carried far enough to indicate the most fruitful

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* See Chapter 8

lines along which it can be developed, as will be shown in the next chapter.

Assumptions and Restrictions

In order to minimize the number of cases which must be considered in the following discussion, the metal-catalyzed drying of linseed oil has been selected for study to exclusion of all other catalytic processes. Furthermore, the free radical mechanism of oxidation has been adopted rather than an unlikely ionic mechanism.

The following assumptions were made concerning the process:

1. The first step in drying is oxidation of the vehicle.
2. The oxidation step is the rate-determining step.
3. All of the oxygen required for the reaction is supplied by the atmosphere, with no contribution from sources within the vehicle.
4. The effectiveness of a catalyst can be measured by physical changes in the vehicle, as manifested by the Gardner Drop Time (q.v.).
5. Reversible oxygenation of the catalyst is a precursor to the formation of the hydroperoxide intermediate.

General Observations

Facts which assisted in the development of the hypothesis, or which must be explained by it, consist of:

1. The electronic configurations of the various metal ions have been established from spectroscopic data; they appear in Figure 24.
2. In the periodic arrangement of the elements, a general tendency toward orbital symmetry* is noted with the result that in the case of the d shell there are three favored configurations: a) no d electrons, b) five electrons in five different orbitals, or c) ten electrons in the five orbitals. **

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* See References 48, 123, and 140.

** The 4s electrons do not enter into the discussion; consequently, the conventional representation of the metal as the ion is used throughout this chapter.

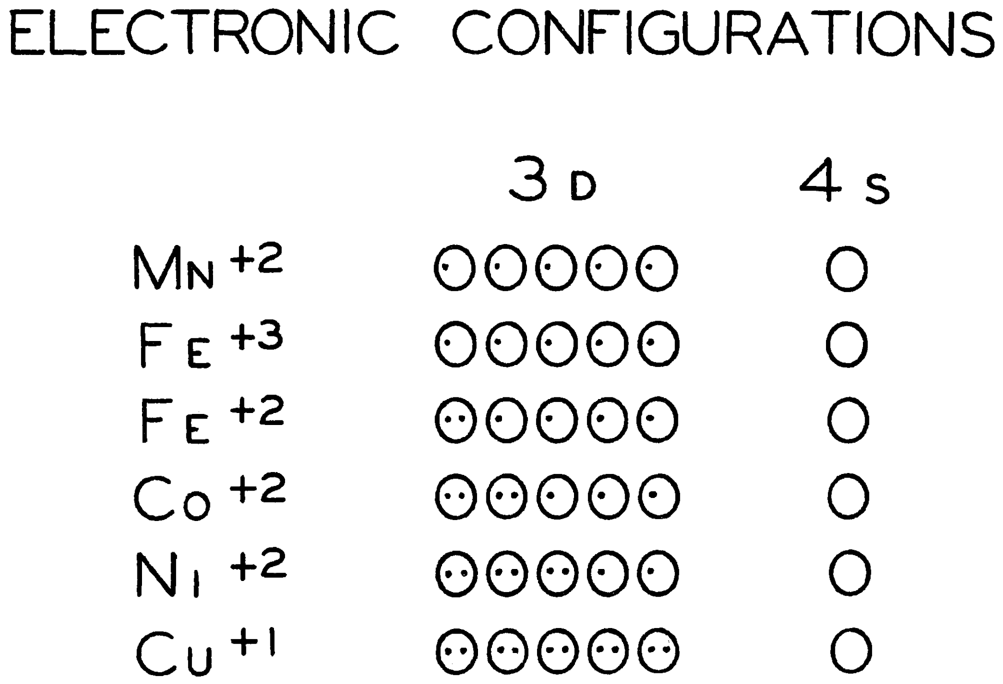

Figure 24.

3. Peculiar redox characteristics resulting from this phenomenon are that ferric ion is more stable than ferrous, that copper exists readily in the monovalent state, that the manganic (+3) ion is converted readily to a +2 or +7 valence, and that the +3 valence of nickel is a rarity.

4. Complexing changes the redox characteristics of the ions in the group considered here (Table II).

5. Strongly basic diamines reduce the efficacy of cobalt and manganese catalysts.

Electronic Mechanism

Let us consider the situation involving uncomplexed ions. From Figure 24 we shall attempt to predict which ion would make the most active catalyst.

Statistically, the manganous ion has a 25% better chance of attracting an oxygen molecule (via one of its π electrons) than does its nearest competitor, ferrous ion. This results from the fivefold degeneracy of the d orbitals of manganese. Ferric iron has the same statistical advantage, but insufficient potential to be oxidized above a valence of three to permit it to be a catalyst.* Ferrous iron enjoys a statistical advantage over the remaining metal ions in the transition group, and might be expected to be a strong catalyst as a result.

However, experience teaches that neither manganese nor iron are as effective as the cobalt ion which possesses only a threefold degeneracy of unfilled 3d orbitals. Clearly, the explanation involves some effect not yet considered.

Reference to the uniform atomic plan conceived by nature supplies the answer. In the assemblage of elements that constitutes our periodic table one can find only two cases in which an s electron is not endowed with less energy than a p electron of the next lower

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* Under the conditions normally encountered in linseed oil drying.

principal quantum number. These cases are when the d shells are one electron short of being a) half-filled*, and b) completely filled**. They give rise to the favored configurations, the attainment of which results in lower energy than one would expect for the metal in question.

These energetic features are superimposed on statistical factors governing the number of reversible unions with oxygen. As a corollary, one might expect to find the energetic requirements for the addition of an electron to a favored configuration somewhat higher than the normal energy associated with a 3d orbital.

The reason for the reluctance of manganese to assume a +3 valence, despite its statistical advantage, is that the favored configuration of five electrons in five orbitals must be destroyed*** in the process.

The passivity of iron and its extreme willingness to enter the trivalent state are manifestations of the same phenomenon. Iron has both the statistical and energetic features which are conducive to union with oxygen, but the requirement that the process be reversible has not been met owing to the fact that the oxygen atom**** on leaving carries both electrons with it. Redistribution of the remaining five 3d electrons in the now ferric ion occurs with the favored configuration as a result. This loss of an oxide ion is the result of heterolytic bond cleavage, rather than the homolytic ruptures which characterizes

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* Chromium, which has the configuration $3d^5 4s$ instead of $3d^4 4s^2$ is an example.

** Copper, whose configuration is $3d^{10} 4s$, not $3d^9 4s^2$, is shown in Figure 22.

*** This is true regardless of whether oxidation is viewed as the loss of an electron or as the formation of a covalent bond with a more electronegative element, in which case an electron is added.

**** Actually, the oxygen molecule is involved. The electronic picture is the same.

free radical reactions.

Cobalt offers the right combination of statistical and energetic features. Not only does the cobaltous ion possess three degenerate forms of the one-electron orbital, but it is characterized further by the fact that at no time during the redox process is a favored configuration approached. Consequently, this "inertial energy" is not required in the acceptance of the oxygen nor in its subsequent loss to the vehicle.

Upon reaching the configuration of nickel the two effects work together to render the ion impotent as an oxidizing catalyst*, for the statistical factor has been reduced to two. Moreover, the filling in of the 3d orbitals has progressed to the point at which the attachment of one oxygen with its electron results in the configuration, $3d^9$. Having seen that this configuration is sufficient in the case of copper to induce the capture of the tenth electron, the surmise that nickel, with a nuclear charge only 1/30 less than copper, can take on a second oxygen with a minimum expenditure of energy is logical. The observation that nickel is unique in its avoidance of a +3 valence results from the $3d^9$ configuration which it would be forced to assume.

The Effect of Complexing

If a way can be found in which the electronic energy requirements of the 3d orbitals can be lowered simultaneously with the retainment of a favorable statistical advantage, drastic increases in the number of reversible unions with oxygen can occur. This is exactly what happens in complexing, particularly when only the partially

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* As contrasted with nickel-catalyzed oxidations and reductions in which the 4s electrons participate.

coordinated species are prevalent. In the case of cobalt, the insertion of one nitrogen atom with its pair of electrons destroys the active cobalt configuration and tends to reduce the efficiency of the catalyst. If two nitrogens are introduced into one cobalt atom, the result will be a configuration in which one lone electron will occupy a 4p orbital and thus will be susceptible to irreversible ionization. This accounts for the stability of trivalent cobalt when complexed. Further complexing ultimately forces this electron into the 5s orbital where it has even more tendency to ionize.

Having seen that the motion of an electron into and out of an orbital is facilitated if two filled orbitals are present as a bulwark against the attainment of a favored configuration, one can predict that the addition of two electrons to manganese via the complexing route will remove the electronic energy barrier operating against the uncomplexed metal. The new configuration will be identical with that of uncomplexed cobalt; moreover, the energy requirements involved in the gain and loss of electrons will be less than in the case of cobalt owing to the lower nuclear charge on the manganous ion.

The effect of the nuclear charge cannot be emphasized too highly. Not only does it influence the activation energy required for the formation of the activated complex*, but it is the driving force behind the attainment of a favored configuration. In the case of manganese versus cobalt this means that not only will the monoammine possess greater oxidizing potential than cobalt; but also the diammine, with its $3d^9$ configuration, will not possess nearly so much reserve

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* Note that complex is used here in the kineticist's sense. It will have the structure: $-O-O-MeX_2$.

affinity for the tenth electron as does the isoelectronic* nickel ion which is three units heavier. Consequently, the diammine may have some oxidizing ability although it may be inferior to the monoammine.

The effect of the nuclear charge is to permit the manganese monoammine to be a much better catalyst than the isolectronic cobalt. It is the cobalt configuration, rather than cobalt, itself, which is believed active in catalysis.

Up to a point, the characteristics sought in a complex catalyst are the attainment of the cobalt configuration and a lowering of the energy requirements for movement of electrons into and out of the orbitals. An interesting corollary of this hypothesis is that a vanadium diammine should prove to be an even more potent catalyst than the postulated manganese monoammine. Scandium, too, is of interest as a candidate for future complexing studies; for the triammine of that metal is isoelectronic with cobalt.

Lowering of the energy requirements of the orbitals cannot be carried on indefinitely; for complexing cannot be carried past the alkali metals. Even if the limiting case, in which no energy is required, were attainable the catalyst probably would be inoperative; for the absence of a catalyst can be viewed as an example of the limiting case.

Anomalies in Experimental Data

One finding which is not in strict accord with the hypothesis is that among the most active complexing agents are included many bidentate amines. The accepted theories of complexing require that

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* Having the same electronic configuration.

chelation occur from coordination with both nitrogen atoms unless structurally prevented from doing so. The fact that the most interesting amines invariably possess structures capable of forming five- or six-membered chelate rings implies that two coordinate covalent bonds participate in the structure of the complex. That they perhaps do not enter into combination at the same time has been proposed as an answer to this objection.

Actually, the traditional view that both nitrogens of a bidentate amine react with the metal may have to be abandoned, especially in cases of weakly basic amines. A precedent for this move has been established in the discovery that silver coordinates with two ethylenediamine molecules instead of one.

A more serious objection to the hypothesis can be advanced on the grounds that it was developed solely from data taken in this laboratory. In addition to the discordant results obtained in early complexing studies, the chemistry of conventional drier metals, themselves, has produced controversial results. Wilborn (171) and one of his predecessors have reported that iron is the second most active metal catalyst, which requires that one avoid any theoretical treatment of the ferrous-ferric electronic configurations which establishes it as inoperative in free radical oxidations. Our further knowledge that the stability of ferrous iron is increased at higher temperatures (and is thereby rendered catalytic) forces us to conclude that electron lability depends to some extent upon temperature. This, of course, is not a new concept; its bearing upon the discussion is that it may help to explain the role of iron as a drier at high temperatures. At least it prohibits one from making unqualified assertions concerning the relative activities of the ions.

CHAPTER 8

THE TEST OF THE HYPOTHESIS

Lines of Approach

For purposes of developing a theory based on the experimental data reported in the first six chapters and which would stem from the hypothesis advanced in Chapter 7, a means of correlating the drying time data with some physical property of the coordination entity was sought.

An inference which can be drawn from the hypothesis is that the relative abundance of the seven possible ionic species* of a given coordination entity would not be the same from one ligand (amine) to another. A strongly basic amine would be characterized by a distribution in which the more highly coordinated species would prevail; a weakly basic amine would complex much less extensively.

Throughout the entire range of possible species the coordination tendencies observed by Werner would prevail to the extent that the diammines would exist at the expense of the mono- and triammines in the case of weak ligands, and the hexammine would be preferred over the pentammine in systems containing strong ligands. In the absence of mitigating factors the even numbered ammines would prevail. This would be true especially in the case of bidentate amines.

The foregoing discussion has been based on the behavior which would be expected of a normal system (i.e., one containing ligands whose structural features enable it to follow the normal course of complexing).

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* But only five possible covalent species since two of the coordination positions are occupied by the negative group.

However, those amines which promote the activity of manganese (and generally of iron) have been shown to possess a resonant structure which chelates with the metal, thus shielding the second coordination position from another ligand; but the chelate then proceeds to relinquish its hold on the metal to the extent that its requirement at any given instant is just one orbital of the metal. Structurally, the even-numbered configuration is retained; but electronically, the monoammine configuration exists.

Of course, other factors may be operating to distort the normal pattern of complexing. Since we are dealing with an equilibrium system, the amine concentration has an important bearing on the relative abundance of each species. The inability of an amine to fit into the normal stereochemical pattern may alter the structure (and hence the orbitals used in bonding). This possibility has been discussed earlier*.

By means of magnetic susceptibility measurements the proof of the above hypothesis may ultimately be obtained. Until such a time as other physico-chemical measurements may indicate that a study of this nature is warranted, the decision was made to initiate a research program in which one of the additive properties of solutions of complexes would be measured. Accordingly, a listing was made of the possible means by which this could be done, and of the obstacles which would be met either in the gathering of the data or in their interpretation in the light of the experimental results already on hand.

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* Page 52. See also References 100-2, 106, 107, and 131.

Electrical Methods

1. Bjerrum's Method.

The ideal experimental approach to ascertaining the extent of complexing is available, provided one confines his researches to aqueous solutions. When Jannik Bjerrum (28) conceived the idea of using the glass electrode in complexing studies, he provided himself with a research program which has steered a generation of his students to their doctorates, and has provided several eminent scientists with material for doctoral programs (29, 30, 83, 84, 99).

Despite the fact that Bjerrum's method is not applicable to organic systems, it is outlined briefly in Appendix VIII in the hopes that it will stimulate a discussion on how its counterpart in aprotic media can be developed. A means of measuring pA directly is needed.

2. Polarography.

Redox methods, in general, ultimately may take over the role of evaluating catalysts, for no serious doubt exists that the redox potential of a given ionic couple is a direct measure of its ability to catalyze a given reaction. Too high a potential means that the lower valence state is too highly stabilized for optimum performance; too low a potential implies that the higher valence state is favored. However, they do not provide the kind of information desired here.

Redox studies have been made by numerous workers (88, 91, 104, 105, 116, 139), most of whom studied aqueous systems by means of the polarograph. Despite the interest which would accrue to an extension of this work to organic media, the experimental difficulties inherent in any electrical method are overwhelming. In addition, the information gained from a redox method does not permit the calculation of successive complexity constants, for it brings to light properties of the system as a whole rather than of the components thereof.

3. Binding Energies.

Whether determined from spectroscopic data, from thermodynamics, or by electrostatic theory, binding energies of the electrons should not be overlooked as a source of information concerning the energy relationships existing between coordination entities and their parent compound. Considerable fundamental data have been compiled by Pauling (121) and Russell (110, 135).

4. Radioactive Indicators.

The equipment for tracing the path of radioactive material through a reaction sequence is available; in addition, cobalt 60 is one of the standard items offered by the Atomic Energy Commission. These facts point to the desirability of drawing up a plan for the determination of dissociation constants by a radioactive indicator method (41).

5. Conductance Measurements.

Conventional application of conductimetric measurements would provide data on the possible existence of ions after the extent of complexing had exceeded four ligand groups. Information of this nature was not deemed necessary at this time, however.

Spectrophotometric Methods

Equilibrium constants for the formation of complexes have been determined spectrophotometrically with a degree of success which depends on the number of species in solution. The reaction of copper with glycine has been studied successfully (128), and many other examples exist of qualitative studies; but by far the most useful spectrophotometric method is that based on the principle that no two complex species of a given coordination entity will possess light absorption peaks at the same wavelength. This is discussed in the next paragraph.

An approach adaptable to organic systems is that of Job (70, 81, 82). Unfortunately, this method is not amenable to quantitative study of systems containing as high as six different complex species, and was not considered further at the time this work was initiated. It should be re-evaluated in the light of the postulate that only four different complex species exist in non-ionizing solvents, in which case the relative amounts of each species may be obtained directly from absorption curves. The accuracy of this method for the purpose just described is doubtful.

Determination of Colligative Properties

Because of the novelty of applying the colligative property laws to the case at hand, the decision was made to exploit the following observation, if at all possible:

If a colligative property of a binary solution of known composition is determined, a relationship can be established between the concentration of solute (the amine in this case) and the magnitude of the property. Regardless of whether the solution is ideal, the established relationship will permit the effective amine concentration to be determined in any system.

Now if a third component is added to the system, two effects will be felt: 1) the magnitude of the property will tend to increase owing to the addition of a new component; and 2) the magnitude of the property will decrease in direct proportion to the number of amine molecules which are removed from solution by the new agent.

This is the theoretical basis of the use of a colligative property as a means of determining the extent of complexing in solutions of varying amine concentration. Through the use of a more direct, but less versatile, method than that of Bjerrum, the necessary information can be obtained from which the successive complexity constants can be obtained*.

The selection of the colligative property method of determining the extent of complexing has opened new vistas in complex chemistry, but does not promise to test the hypothesis advanced in Chapter 7. An earlier concept of the effect of the amine structure on complexing was that some ligands preferred to form monoammines rather than to follow the normal course of reaction to the diammine; and despite the fact that it has been superseded by the hypothesis of partial chelation, in order to explain the efficacy with manganese of cyclohexylamine, dicyclohexylamine, and other non-resonating structures, this stereochemical explanation may have to be revived. If so, then the measurements proposed here will have a profound bearing on the problem.

In spite of limitations in the employable concentration range, the method involving the measurement of a colligative property were scrutinized closely. Regardless of the one selected for study, additional restrictions would be imposed by one or more of the following:

1. Solubility,
2. Solvation effects,
3. Association or dissociation,

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* See References 71-3 and 108 for other problems involving successive complexity constants.

4. Volatility,
5. Accuracy of results,
6. Operational difficulties,
7. Sample preparation,
8. Temperature control,
9. Temperature range,
10. General applicability,
11. Practicality,
12. Application to the hypothesis.

Consideration was given first to the most rudimentary and least complicated of physical measurements; namely, the determination of vapor pressures. If the vapor pressure profile of a solid ammine is determined (27) the relative stability of each of the coordinated species can be calculated from the relation:

$$Me^{++} + nA \longrightarrow Me\,(A)^{++} + (n-1)A \longrightarrow Me\,(A_2)^{++} + (n-2)\,A$$

$$\longrightarrow Me\,(A)n^{++} + (n-3)\,A \longrightarrow \text{etc.}$$

where $k_1 = \dfrac{[MeA^{++}]}{[Me^{++}][A]}$

$$k_2 = \frac{[MeA_2^{++}]}{[MeA]\,[A]} = \frac{[MeA_2^{++}]}{k_1\,[Me^{++}]\,[A]^2}$$

$$k_3 = \frac{[MeA_3^{++}]}{[MeA_2^{++}][A]} = \frac{[MeA_3^{++}]}{k_1k_2[Me^{++}]\,[A]^3}$$

through the use of pressures (or fugacities) in place of concentrations. It is obvious that each successive equilibrium constant varies inversely as the pressure; and the overall constants, as a power thereof; i.e.,

$$K_3 = k_1k_2k_3 = \frac{[MeA_3^{++}]}{[Me^{++}][A]^3}$$

These complexity constants could be used in the computation of the relative abundance of each coordinated species present in the coordination entity if the limitations imposed by the phase rule were not felt; i.e.,

$$F = C - P + 2,$$

in which the number of degrees of freedom, F, is found by adding 2 to the number of components, C, and subtracting the number of phases, P. The limitation imposed here is that the number of phases cannot exceed three (of which the vapor of the ligand is one) if one degree of freedom is to be retained. Therefore, unless the coordinated species form a solid solution*, no more than two of the species can coexist.

For this reason, the determination of successive complexity constants by vapor pressure measurements on solid complexes was abandoned.

Determination of the vapor pressures of organic solutions was considered next; for in this case the number of phases is two, leaving two degrees of freedom. One degree of freedom would be the amine concentration; the other, the vapor pressure.

The difficulties associated with this method are of the operational variety. First, a relatively nonvolatile solvent must be selected; secondly, vapor pressure must be read accurately in an extremely low pressure system in order to embrace amine concentrations of the order

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* Which is doubtful since their stereochemical patterns are different.

involved in complex catalysis. Despite the fact that the method has enormous theoretical and practical value, it was not considered further at this time.

Measurement of osmotic pressure was abandoned because of similar difficulties. Distribution coefficients of amine between two immiscible liquids can be measured with relative ease (97), but in this particular case the method cannot be employed because the second liquid would have to be polar if an aprotic medium were used as the reaction phase.

Vapor-liquid equilibria offer a novel means of determining reaction equilibrium concentrations; however, the accuracy obtained with an apparatus of this type is not of the highest order owing to operating difficulties. Further, the data would have to be taken at temperatures considerably above room temperature in order to insure against loss of material on sampling.

The method of boiling point elevation (160) was objected to on the grounds that fluctuations in atmospheric pressure would constitute a serious drawback to the gathering of accurate data. Operation under reduced pressure, using a precision manostat, would resolve this difficulty as well as the objection against taking data far above the ambient temperature. Nevertheless, this approach was discarded.

The process selected as the one most likely to yield consistent, accurate data at a temperature not too far removed from that encountered in the drying of oleoresinous films was the cryoscopic method, details of which are supplied in the next chapter. Preliminary results on the selection of the solvent are reported below.

Selection of the Solvent*

Inasmuch as data were desired on a system uncomplicated by solvation effects, the use of a polar solvent was ruled out from the beginning. The information contained in Table II (q.v.) shows that the use of a compound such as carbon tetrachloride would not be advisable owing to the residual coordination potential of the chlorine atoms. In short, any compound in which carbon is linked to an atom other than hydrogen or another carbon was not considered. This left only the hydrocarbons.

At first benzene was excluded owing to the unsaturated π electrons existing in its structure; later its use was dictated by solubility problems, but the hope is entertained that ultimately it can be discarded in favor of a fully saturated hydrocarbon, or else that proof can be offered that its use is not subject to complications.

Of the saturated hydrocarbons, cyclohexane was chosen because of its convenient freezing point (6.5°C.), its high molal freezing point depression** (20°C.), and its availability in a spectroscopic grade. After several series of determinations using cyclohexane as the solvent, a serious limitation was encountered in the finding that its solvent powers were much lower than those of benzene. Furthermore, its high K_f value was found to be a liability rather than an asset when an accurate means of measuring temperatures was developed (see Chapter 9), for it permitted a larger spread of temperatures within a given series than deemed consistent with the precision obtainable with the method.

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* See References 66 and 126.

** This will be referred to as K_f. See Appendix IX for K_f values of other solvents.

As a result, the use of both cyclohexylamine (for limited application in extremely dilute solutions) and benzene (for general use, including high concentrations of amine) has been adopted. Work has not progressed to the point at which one can state with certainty that results obtained using one solvent are interconvertible with the other.

Additional details of the method are given in the next chapter.

CHAPTER 9

CRYOSCOPY

Practical Significance*

In Chapter 8 the importance of determining the extent of complexing as a means of characterizing the amines used in the acceleration of catalysis was pointed out. In addition, the technique of determining one of the colligative properties as a means to this end was indicated as the most desirable of the possible methods; this was narrowed down to the selection of cryoscopy in non-aqueous media as the most fruitful line of attack. For purposes of demonstrating that the method is capable of providing useful fundamental data a trial run was made with silver acetate. Later a group of experiments was performed using amylamine as the ligand, cobalt and manganese as the metals, and cyclohexane and benzene as the solvents. Extension of the work to other ligands, metals and solvents will constitute the second phase of the work which is planned for the near future.

To the best of the author's knowledge, the cryoscopic method has not been employed in its present capacity by others. It has been used in molecular weight determinations (25, 125), in differentiating between inter- and intramolecular hydrogen bonds (3), in determining other facets of molecular constitution (9), in studying geometric isomerism (22, 34, 36, 120, 150b) and other steric relationships (61), in systematizing the data on homologous series of compounds (64), in the proof of the existence of free radicals (68), in establishing the

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* See References 4, 95, 141-151, and 159, in addition to those given detailed mention.

conditions of polymer formation (119, 125), in calibrations of temperature-reading devices (143a), in studying phase transformations (143b, 146, 147, 148), in analytical methods (150b, 153, 170), in determining thermodynamic data (170), in establishing purity standards (67, 98, 158) and in studying reaction kinetics (120). Its application to the determination of the extent of complexing appears to have been overlooked.

Materials

Normal amylamine was provided by Sharples Chemical Company in better than 98% purity, and was used without further treatment. The cyclohexane used in the earlier runs was of spectroscopic grade; the benzene, with which later, more reliable data were obtained, was Baker's C.P. grade which had been dried for a minimum of three days over sodium and distilled through a 4' helix-packed column at a 40:1 reflux ratio. The fraction boiling from 80.0 to 80.1°C. (uncorrected) was used.

Manganese chloride was prepared by dehydration of Fisher's C.P. grade tetrahydrate in an Abderhalden drier at the boiling point of nitrobenzene (211°C.) using the full vacuum of a Welch Duo-Seal pump and P_2O_5 in the desiccation chamber. Cobalt acetate was obtained by dehydration of the C.P. tetrahydrate at 110°C. in a vacuum oven.

Equipment*

A Beckmann freezing point apparatus was employed in the gathering of the data reported in Tables XXV and XXVI. Stirring was accomplished by a vacuum-operated windshield wiper. While a modified Beckmann

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* See References 1, 5-7, 35, 44, 65-67, 77, 87, 96, 98, 134, 142, 149a, 157, 162, and 169 for descriptions of equipment used by others.

apparatus (Figure 25) was far more satisfactory, this was soon supplanted by a much improved apparatus (Figures 26 and 27). The reason for the change, and suggestions for further improvement will be given later in the chapter.

Thermometry*

Initially, the traditional Beckmann thermometer was used. The fact soon became apparent that the precision of the measurements (0.001°C.) was not matched by their accuracy owing to a temperature lag at the time of crystallization; as a result the mercury thermometer was discarded in favor of resistance thermometry.

A platinum resistance thermometer of proper dimensions and heat capacity was unavailable; however, a type 15A thermistor (26) kindly provided by the Western Electric Company was used satisfactorily in conjunction with a Mueller Bridge (Figure 27) capable of indicating resistances up to 100 ohms with a precision of 0.0001 ohm. A 103-ohm auxiliary resistor of manganin wire was placed in parallel with the thermistor in order to bring the overall resistance of the assembly to a value well within the limits of the bridge. While this expedient reduced the sensitivity of the thermistor, a temperature coefficient of one ohm per degree was obtained with the assembly. Thus, temperature differences as low as 0.0001°C. could be read, but this was necessary only in very dilute solutions.

Calibration of the bridge had been done by the manufacturer. Results are reproduced in Appendix X.

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* See References 24, 26, 35, 42, 67, 77, 87, 98, 142, 149a, 157, 158, 159.

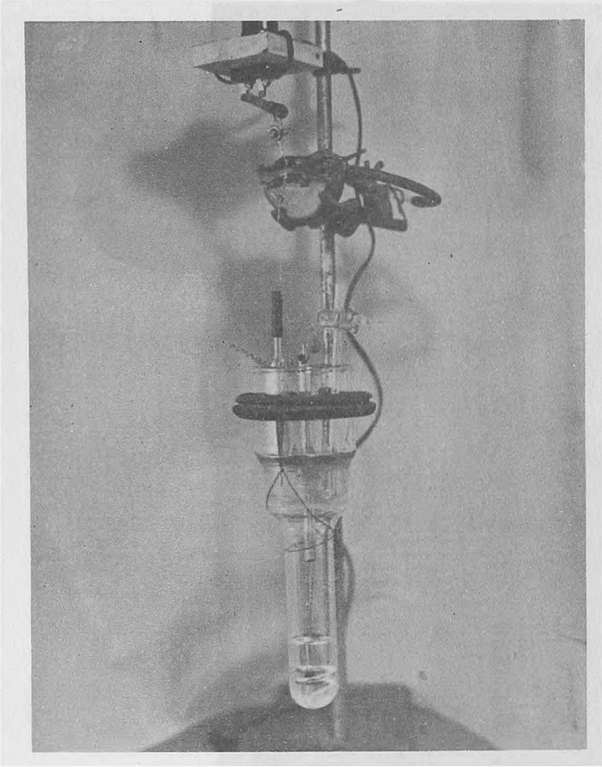

Figure 25.

Modified Beckmann

Freezing Point Apparatus

Figure 26.

Improved

Cryoscopic Apparatus

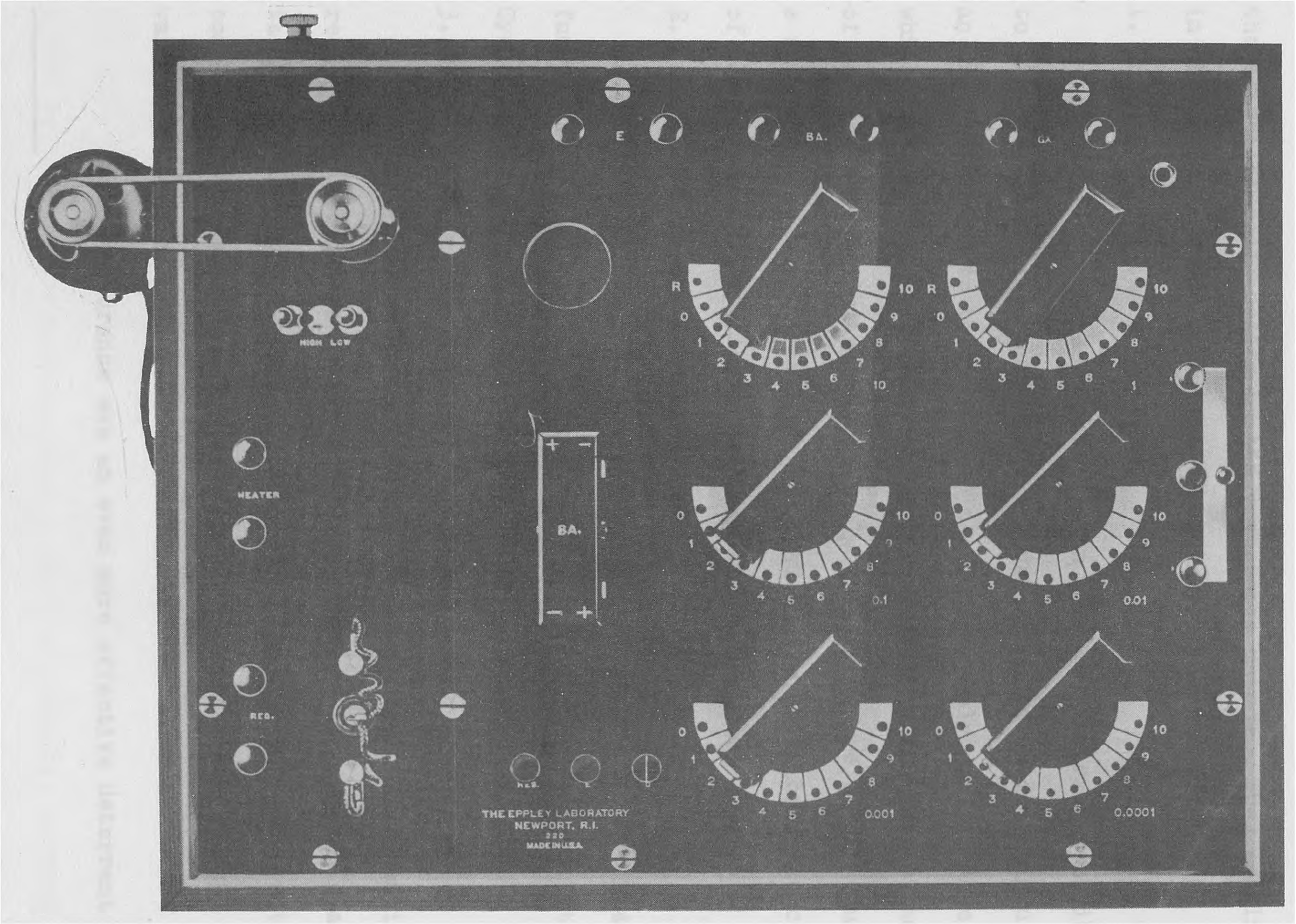

Figure 27

Mueller Bridge

General Precautions*

The following obstacles were encountered in the measurement of the extent of coordination by the cryoscopic method. They are listed in the order in which they were recognized.

1. Solubility of the Metal Salt.

Inasmuch as the concentration of dissolved salt contributed to the freezing point depression, its value had to be determined with an accuracy equal to that obtainable with the analytical balance on which the weighings were made. For difficultly soluble salts the accuracy of the method was limited by the analytical procedure used. Consequently, a salt whose solubility was not exceeded by the equilibrium concentration of the uncomplexed species** was required.

2. Solubility of the Ligand.

Many of the most interesting amines possessed more than one functional group which seriously lowered their benzene solubility. Cyclohexane was an even poorer solvent than benzene.

3. Variety of Ligands Available.

Weakly basic amines, which did not possess the potential required to coordinate with the metal, could not be examined quantitatively. In these cases a qualitative expression of the extent of complexing was used in making comparisons of structural effects of various classes of amines.

Steric hindrance was an even more effective deterrent to

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* See References 60, 92, 117, 141, 143, 144, 145, 150a, 152, and 165.

** All of the complexed species studied to date, with the exception of silver, were soluble. Cobalt acetate and manganese chloride appeared satisfactory from the standpoint of the solubility of the uncomplexed material.

complexing potential. In benzene solution, triamyl amine appeared to be inert in spite of its basic strength. Again, a qualitative expression of its behavior must be resorted to in order to compare it with primary and secondary aliphatic amines.

As insight into the problems encountered in the preliminary screening of amines available for cryoscopic study can be gained by reference to Table XXIV (Appendix XI).

4. Purity of the Materials.

Purification of the solvent has been described. The metal salts possessed acidic odors prior to dehydration, but their purity was not questioned inasmuch as they were taken from newly-opened containers of the best grade of material available. The amylamine had been distilled through an efficient fractionating column prior to shipment, and contained an insufficient amount of amyl chloride to produce oiliness in hydrochloric acid solution, although a slight odor of the chloride was detected. Its assay was 98½%.

The anhydrous metal salts were stored and transferred in a specially constructed dry box (See Figure 28). This was necessary in order to prevent any water from coordinating with the metal.

5. Ideality of the System.*

Primary amines did not produce ideal solutions owing to association of the solute molecules. From 0.1 to 0.5 molal, amylamine was 12% associated in cyclohexane, while in benzene the figure was about 3.5%** Pyridine and cyclohexylamine behaved abnormally, presumably as a

---

* See References 60, 79, 92, 130, 141, and 165.

** Based on thermistor values. The non-linearity of the temperature dependence prevented this figure from being obtained with extreme accuracy. This was not serious, inasmuch as empirical values were used in later calculations.

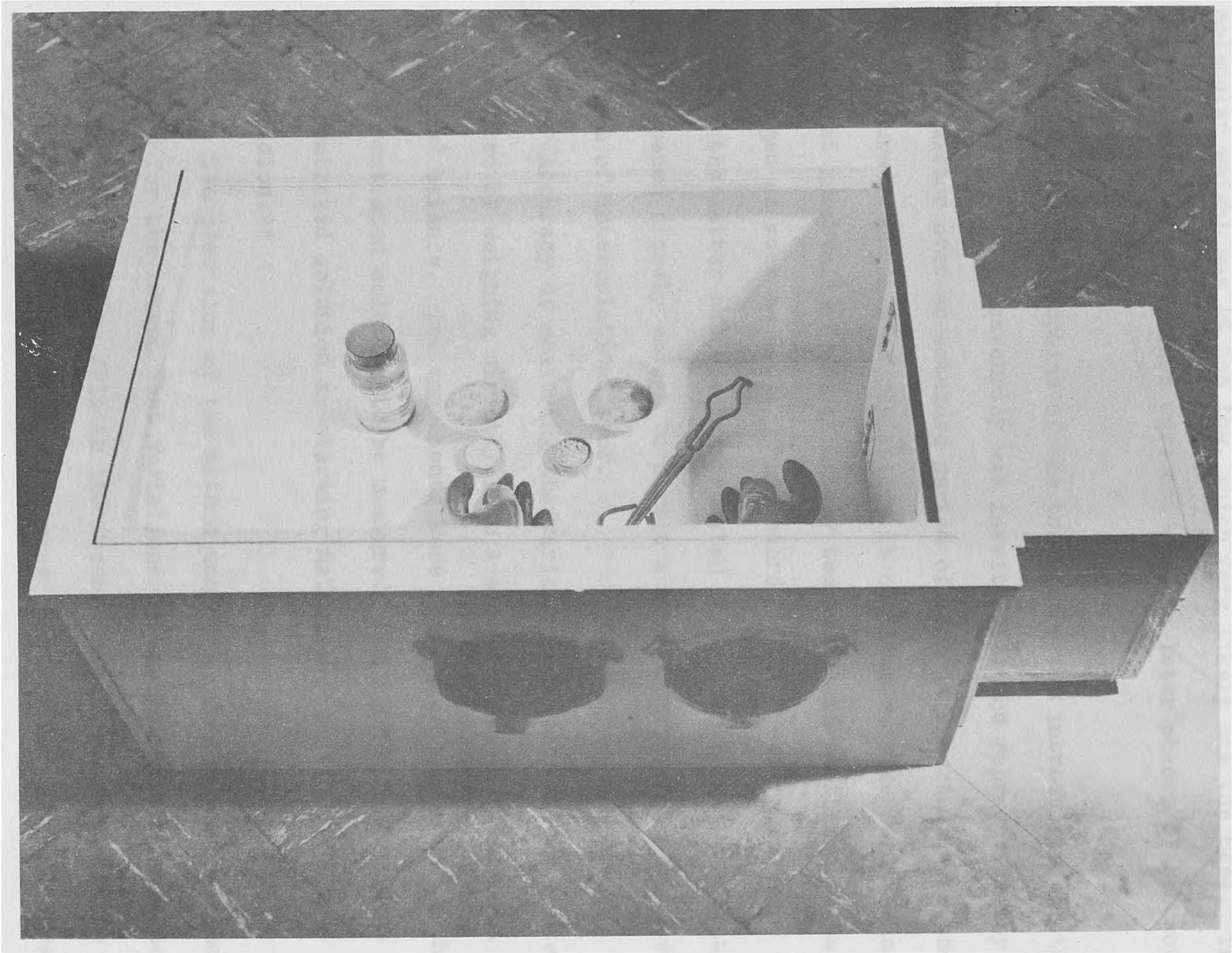

Figure 28

<u>Dry Box</u>

result of mixed crystal formation. Triamylamine behaved as if its molecular weight was 4% too low, which very likely was the case. The last three mentioned amines were not used in later phases of the work.

6. Accuracy.*

With the adoption of the thermistor the introduction of two possible sources of inaccuracy was inevitable: the reproducibility of any thermistor over an extended period of time is uncertain, and the temperature dependence of resistance is not linear. The former was checked at intervals of approximately two weeks and at this date has not changed as much as 0.001°C. in recording the freezing point of pure benzene; the latter has been compensated for by the use of calibration points spaced closely enough to permit a smooth curve to be drawn with a minimum of interpolation error.

Accuracy of measuring the various components of the system was assured by weighing directly into a closed container, using an analytical balance. The components were charged in the ratio of the most concentrated solution to be measured, and dilutions were made using the concentrated solution as starting material.

7. Precision.**

The precision of the method unquestionably was much higher than necessary for the reason that variations in the freezing points due to equilibrium shifts were felt in the second decimal place while the freezing points were measurable to three places. The chief deterrent

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* See References 60, 79, 89, 92, 117, 130, 137, 150a, 152.
** See References 24, 42, and 89.

to high precision was the phenomenon of supercooling which when excessive made the point of intersection* of the cooling curve and the crystallization curve somewhat doubtful. On these occasions the determination was discarded.

8. Stability of the Complex.**

The forewarning that cobalt complexes are susceptible to oxidation was responsible for the precaution that a nitrogen atmosphere was maintained over all solutions of complexes. This, combined with the purity of the solvent, assured that the metal remained in its lower valent form throughout the investigation.

9. Standardization.***

So long as the Beckmann thermometer was employed, a check on the experimental K_f could be made by comparison with the theoretical value. Similarly, the exponential temperature coefficient of the thermistor would have permitted the application of theory to experiment, had not the auxiliary resistor been introduced into the system. That the temperature-resistance relationship of the assembly was neither linear nor logarithmic is shown mathematically in Appendix XII; that the relationship appeared to be linear over a wide temperature range is shown in Figure 28 (Appendix XIII). When the slopes of the straight portions of each curve were plotted against sensitivity of the assembly (ohms per degree) interpolation to the value at which the sensitivity was exactly 1.0 ohm per degree showed that a 103-ohm auxiliary resistor was required. This was soldered to the thermistor leads and remained

---

* See later under Operation.
** See Reference 160.
*** See References 138 and 151.

unchanged throughout the investigation.

Unfortunately, on accurate standardization of the assembly versus solutions of diphenyl in benzene (and also with the amine solutions) the non-linearity of the curve was apparent. The calibration curve was plotted on 24" graph paper, from which conversions of resistance to molality were made. Inasmuch as the apparatus will be changed this curve has not been reproduced.

10. Equilibrium Shifts.

Taube (160) has pointed out that most complexes equilibrate within a matter of minutes. While this was not the case with the Beckmann apparatus, whose chief drawback was the requirement of at least one day's equilibration (with intermittent stirring) for the determination of each point, it was sufficiently rapid to introduce inaccuracies in early determinations using the new apparatus; for the standard technique consisted of allowing the solution to equilibrate in a thermostatted cabinet at 30°C. for several days, after which the cooling curve was run.

A serious limitation of the cryoscopic method results from the non-isothermal conditions encountered in the variations in the amount of freezing point lowering. A concentrated amine solution freezes several degrees lower than a dilute solution; therefore, equilibrium shifts are more pronounced in the former. The tentative solution to this problem is pointed out in the section devoted to operational procedure.

11. Supercooling.*

When the amount of supercooling was excessive (greater than 1.0°C.) the point of intersection of the curves was less precisely determined than when a normal (ca 0.5°) amount of supercooling occurred. Suggestions

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* See References 161 and 170.

for the elimination of this variable are made in the design of a new apparatus.

Special Precautions

With the establishment of a technique in which an electrical method of temperature measurement was used, the following special precautions were necessary.

Reaction of the thermistor with the amine solution was of chief concern. That this did not occur to a measurable extent was shown by the accuracy with which the freezing point of benzene was obtained at intervals of approximately two weeks.

Conduction by the solution was determined to be non-existent by the simple expedient of observing the absence of galvanometer deflection when the thermistor leads were plunged into solutions of the complex.

Changes in the thermistor characteristics were checked at intervals using pure benzene and solutions of diphenyl in benzene. No discrepancies were noted.

Operation

The modified Beckmann apparatus was operated by charging the amine solution, sealing the apparatus with mercury, determining the freezing point, and repeating the steps after the addition of a weighed amount of metal salt. Equilibration occurred at room temperature owing to the absence of a means of thermostatting the apparatus.

The improved cryoscopic apparatus, which consisted of a 2-ounce bottle equipped with a Teflon-lined screw cap, was designed to eliminate errors resulting from solvent losses, the presence of air, inefficient stirring, contamination by mercury, insufficient time of equilibration, temperature fluctuations during equilibration, and the entrance of moisture. The procedure adopted with this apparatus is outlined below:

> A solution (I) of amylamine in pure benzene was prepared under nitrogen and a sample set aside in a 2-ounce bottle equipped with a glass-encased magnetic stirrer. The solution was about 1.5 molal.
>
> Solution II was prepared by adding sufficient cobalt acetate or manganese chloride to produce a molality of about 0.1. A sample of this was transferred to a nitrogen-filled bottle equipped with a magnetic stirrer.
>
> Solutions III to VIII were prepared by weighing varying amounts of II into tared, nitrogen-filled bottles; and an accurately weighed quantity of benzene was added to bring the volume to 25-30 ml. Molalities ranged from 1.2 to 0.05. Each bottle was equipped with a stirrer and a Teflon-lined cap.
>
> The samples were stored for a minimum of four days in a refrigerator maintained at 7 °C. ± 1°C., after which cooling curves were run in quadruplicate, the sample being warmed to 5-7° between each determination. In order to determine the freezing point, the bottle was opened momentarily in order to fit it with a cap through which passed the thermistor leads. Connection with the Mueller Bridge was established with soldered joints. The Brdige was thermostatted at 27°C. ± 0.1°.
>
> Stirring was effected by means of a rotating bar magnet mounted beneath the refrigerated well into which the thermistor-equipped bottle was inserted. The bath temperature was kept at 0°C. by an ice bath except for the more concentrated solutions which required the addition of salt to the ice bath.
>
> Timing of the rate of cooling originally was done by an electrical impulse counter attached to the vacuum-driven wiper. Later, a chronoscope provided by the Psychology department was used. A stopwatch was unsuitable for the purpose owing to the necessity of making instantaneous readings at given resistance settings.

> During cooling the Mueller Bridge was set at a resistance in advance of that corresponding to the temperature of the solution. The deflection of the galvanometer was noted at short intervals, and the time recorded when it zeroed. After crystallization the magnitude of the advance of the bridge setting was reduced.
>
> Time-resistance plots were made on cross-ruled paper on a scale of one degree (one ohm) per foot. This permitted resistances to be read to 0.001° by estimation. Effective amine concentrations were read from the calibration curve.

The above procedure was used to provide data on the extent of complexing of amylamine with salts of cobalt and manganese. Results of these determinations, as well as earlier determinations on silver acetate and cobalt acetate are given in the following section.

Results

Silver acetate was the first salt studied because of its low coordination number. Data on the extent of complexing in the amine concentration range from 0.029 to 0.166 molal showed that the method was feasible. Many of the errors were brought to light in this series, especially the temperature lag of the thermometer. Results are given in Table XXV.

Table XXV

SILVER ACETATE CRYOSCOPY

$[A]$	pA	$\bar{n}$
0.166	0.78	1.76
0.132	0.88	1.75
0.108	0.96	1.42
0.089	1.05	1.57
0.030	1.52	1.28
0.029	1.54	1.18

Solvent: cyclohexane
Apparatus: Beckmann

Before modification, the Beckmann apparatus was used in determining the extent of complexing of cobalt acetate, with the results shown in Table XXVI. Again, these have been inserted chiefly because of their historical interest, for they showed for the first time that six coordination positions were not available to the ligand owing to the occupancy of two positions by the acetate groups. Furthermore, they show that cryoscopy in cyclohexane produces results which are identical with those obtained with benzene solutions, at least within the limits imposed by the fact that equilibration temperatures were not known in the first series.

Table XXVI

COBALT ACETATE CRYOSCOPY I

[A]	pA	$\bar{n}$
.387	0.41	3.46
.356	0.45	3.49
.341	0.47	3.58
.322	0.49	3.52
.292	0.54	3.44
.269	0.57	3.48
.226	0.65	3.40

Solvent: cyclohexane
Apparatus: Beckmann

The second cobalt acetate series (Table XXVII) is, of course, the more reliable of the two. While the data do not extend far enough into the high pA (low amine concentration) range to permit the so-called formation curve (28) to be drawn, they cover the low pA range sufficiently well to permit the declaration to be made that the maximum number of coordination positions available is four.

Table XVII

COBALT ACETATE CRYOSCOPY II

M_A (tot.)	M_{Me}	$[A]$	M_A (bound)	$\bar{n}$
1.2777	0.1712	0.891	0.387 + 0.171 = 0.558	3.27
1.0680	0.1431	0.730	0.338 + 0.143 = 0.481	3.36
0.7582	0.1016	0.520	0.238 + 0.102 = 0.340	3.33
0.5219	0.0699	0.345	0.177 + 0.070 = 0.247	3.54
0.2614	0.0350	0.173	0.088 + 0.035 = 0.123	3.52
0.1489	0.0200	0.099	0.050 + 0.020 = 0.070	3.50
0.0919	0.0123	0.064	0.028 + 0.012 = 0.040	3.26
0.0492	0.0066	0.035	0.014 + 0.007 = 0.021	3.18

Solvent: benzene
Apparatus: Improved model

The situation with manganese is somewhat different. From Table XXVIII the conclusion can be drawn either that the data are in error by 10% or more, or that a fifth coordination position has opened. No doubt exists that the curve is flattened and $\bar{n}$ shows no tendency to attain the value of 6.

Table XVIII

MANGANESE CHLORIDE CRYOSCOPY

M_A (tot.)	M_{Me}	$[A]$	M_A (bound)	$\bar{n}$
1.3118	0.0762	1.048	0.264 + 0.076 = 0.340	4.46
1.0562	0.0614	0.850	0.206 + 0.061 = 0.267	4.44
0.7717	0.0448	0.610	0.162 + 0.045 = 0.207	4.35
0.5979	0.0347	0.479	0.119 + 0.035 = 0.154	4.60
0.3777	0.0219	0.296	0.082 + 0.022 = 0.104	4.75
0.2229	0.0129	0.178	0.045 + 0.013 = 0.058	4.50
0.2097	0.0122	0.168	0.042 + 0.012 = 0.054	4.42

Solvent: benzene
Apparatus: Improved model

The impact of this finding is obvious. If the data presented here are correct they prove that the behavior of complexes in aprotic media is distinct from that in aqueous solvents. Despite the fact that the ligand does not compete with the solvent for coordination positions, it does not attain as high a degree of coordination at high amine concentrations simply because the negative group has no place to go. It cannot wander off as an anion because benzene does not have the solvent power for the polar group.

This phenomenon is perhaps the best example available of the distinction which should be made between ionization and dissociation. If one single criterion of bond type can ever be used in establishing whether a bond is covalent or ionic* the measurement of the number of coordination positions shows promise of being the answer. If the silver acetate data were more reliable one might conclude that it is truly an ionic compound; for not only does it exhibit the same coordination number in cyclohexane as in water, but its coordinated species do not dissolve in benzene. This was the chief distinction between the results with silver and those involving the transition metals.

The remark is appropriate at this point that all of the manganese and cobalt cryoscopic data were adjusted for the solubility of the metal salt, while the silver acetate data were not**.

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* Seven have been recognized: 1) Existence of isomers; 2) Conductivity; 3) Molecular weight anomalies; 4) Tests for particular ions; 5) X-ray patterns; 6) Boiling points; and 7) The solvent in which the compound dissolves. All are subject to misinterpretation. The method proposed above may be more consistent.

** No turbidity resulted when a nitric acid solution of the ignition residue of the liquor was treated with chloride ion. On neutralization the solution remained clear.

Conclusions

As a measure of the extent of complexing in non-aqueous media the cryoscopic method promises to open a new frontier in the chemistry of complexes. With the information already on hand a long range research program can be built around the extension to organic media of the volumes of data already gathered on aqueous solutions.

The method has an equally strong appeal to the theorist, for it may be the answer to the long-sought question on how to characterize bond types. If so, the fruits of the endeavor reported here will be far sweeter than first envisioned when it was outlined as a means of characterizing the amines used in complex catalysis.

In addition to its proven use in fundamental studies, the cryoscopic method may yet be applied toward fitting certain amines (notably cyclohexylamine, dicyclohexylamine and hexamethylenetetramine) into the hypothesis advanced for the activity of resonant chelate-formers. At present its use is limited by the concentration range available for study; this objection can be overcome by the proposals outlined in the next section which guarantee to open up a pA range of at least two units, corresponding to a 100-fold dilution.

Future Work

The equipment has been redesigned around the Mueller Bridge, the 2-ounce bottle, and a thermistor whose resistance will not exceed 110 ohms at the lowest temperature encountered in the particular series under investigation. By the use of a thermistor of these characteristics a linear temperature dependence will be available through the use of a logarithmic ordinate for resistances. Extreme sensitivity will permit temperature differences of 0.0001°C to be read.

Supercooling will be minimized and standardized by the use of a chilled silver wire or rod to convey heat from the apparatus. Two designs are under consideration: one in which the cooling rod is partially immersed in the liquid, the other in which it contacts a small area of the outer surface of the bottle.

The effect of temperature on the position of equilibrium may be studied by supplementing the use of benzene as the cryoscopic solvent by diphenyl and naphthalene. From these measurements valuable thermodynamic data on the complexing process will be made available.

Extension of the work to other metals and to other ligands is a logical outcome of the work. Any one of a large number of programs can be outlined, and can be directed toward the particular interests of the investigator. For example, several short range programs may be set up for confirming the discovery that only four coordination positions are available with cobalt while five appear to be the limit with manganese. Another would be to study the effect of branching of the carbon chain adjacent to the nitrogen group of the amine; a third would be to ascertain the behavior of ferrous and ferric iron with simple amines. With the improvements planned in the method, extension of manganese and cobalt studies to amines such as Schiff's base can be done.

The fundamental aspects of complexing hold the key to the development of a supercatalyst. While the most economical use of currently available amines and conventional catalysts appears to have been defined clearly (Appendix VII), the bright future of the most inexpensive metal of all (iron) calls for deeper investigation into the electronic phenomena associated with complexing and with oxidation.

Extension of the work to vanadium and to the rare earths would offer unlimited opportunities for fundamental research, if not for practical studies. In all cases an amine addition program would complement the complexing and cryoscopic phases of the work.

The belief is held that the electronic hypothesis of catalysis can be proved or disproved by means of magnetic susceptibility measurements. By permitting a quantitative estimation of the number of unpaired electrons this method can be used to determine unequivocally whether a given chelate requires the full-time participation of two orbitals. A discussion of this method has been avoided in this work owing to the additional scope which would be added to an already varied and lengthy treatise. It is mentioned as a promising long range program which warrants serious consideration in the future.

RRMyers

> Search for the measurable elements among
> your phenomena, and then search for relations
> between these measures of physical quantities.
>
> --A. N. Whitehead

APPENDICES

APPENDIX I

Tentative Agenda

First Technical Conference

Advance Solvents - Harshaw Research Project

Lehigh University May 10, 1950

I. Experimental Techniques

1. First studies in simple oil such as an alkali-refined linseed oil.
2. Drying time recorder.
3. Way of expressing results.
    a. Comparison with standard.

II. Background

1. Work of National Printing Ink Research Institute.
2. Work of Advance and Harshaw.
3. University of Illinois and Pauling's work on complexes.
4. Farmer's work on drying mechanism.
5. Nicholson, Wheeler, biochemists and other workers.

III. Objective

1. To find the type or types of metal complexes which make the most effective drying catalysts.
    a. All types of metals and organic complexing agents should be covered.

IV. Experimental Approach

1. Classification of complexing agents.
2. Measure drying time of a wide variety of complexing agents with a variety of metals.
3. Precautions
    a. Check on whether complex is actually present.
    b. Optimum effect may be found at a low concentration.
    c. Solubility may frequently be a problem.
4. Other desirable properties?
5. Develop theory of mechanism of process.

Those present at the meeting:

For Advance Solvents: Mr. Klebsattel
For Harshaw: Mr. Long and Mr. Hovey
For Lehigh: Dr. Zettlemoyer and Dr. Walker

(see p. 10)

APPENDIX II

Coordinated Metal Drying Catalysts

Key to Names and Classification of Amine Additives

No.	Name	Class
1	n propylamine	111.0
2	butylamine	111.0
3	n amylamine	111.0
4	2 ethyl hexylamine	111.0
5	diethyl amine	211.0
6	di n propylamine	211.0
7	triamylamine	311.0
9	hexamethylene tetramine	344.0
10	N acetyl ethanolamine	211.15
11	triethanolamine	311.1
12	octylphenoxy ethoxy ethyl dimethylamine	311.1
13	stearyl dimethylamine	311.0
14	NN′diethyl cyclohexylamine	331.0
15	aniline	121.0
16	3,4 diaminotoluene	122.0
17	α picoline	341.0
18	morpholine	241.1
19	pyridine	341.0
20	2 amino pyridine	342.0-142.0
21	2 amino pyrimidine	343.0-143.0
22	quinoline	341.0
23	Armeen TD (tallow amine)	111.0
24	Armeed T (tallow amine acetate)	411.5
25	Armeen 18D (octadecylamine)	111.0
26	Armeed 8D (octylamine)	111.0
27	Rosin Amine D (phenanthrene carboxylic acid)	221.5
28	ø β naphthylamine	221.0
29	mono and di heptyl diphenylamines	221.0
30	isopropoxy di ø amine	221.1
31	p hydroxy di ø amine	221.1
32	n nitroso di ø amine	322.0-522.0
33	di ø p phenylene diamine	222.0
34	di β naphthyl p phenylene diamine	222.0
35	di benzylamine	211.0
36	benzylamine	111.0
37	allyl amine	111.7
38	o phenylenediamine	122.0
39	2 nitropropane	511.0
40	dicyclohexylamine	231.0
41	NN′ di n butyl urea	252.0
42	Hemin	344.34
43	o phenanthroline	342.0
44	nitro o phenanthroline	343.0-543.0

No.	Name	Class
45	diazoaminobenzene	223.0-323.0
46	dl leucine	111.5
47	αα' dipyridyl	342.0
48	hematin sulfate	344.14
51	monoamylamine ricinoleate	411.5
52	ϕ guanadine stearate	253.1-223.1
53	2 amino et sulfuric acid	112.2
54	Versene (aq. sol'n. of Na_4)	
55	Versene Fe_3	
56	Ni Na_2 Versenate	
57	Cd Na_2 Versenate	
58	Cu Na_2 Versenate	
59	Sn Na_2 Versenate	
60	Pb Na_2 Versenate	
61	Co Na_2 Versenate	
62	(Versene) Sequestrene AA	312.5
63	Diphenylamine	221.0
64	Tetrabutyl Sequestrenate	312.5
65	Benzidine	122.0
66	s di ϕ carbazide	224.5-254.5
67	Ethylene thiourea	242.2-252.2
68	p Bromo Acetanilide	221.35
69	Me Acetyl Urea	252.5
70	Picolinic Acid	341.5
71	Isonicotinic Acid	341.5
72	Me ϕ Pyrazolone	242.5-342.5
73	NN' bis OH et Aniline	321.1-311.1
74	α NO β Naphthol	521.1
75	Benzyl tri me Amm Butoxide	411.1
76	o dime NH_2 me p C_8 ϕ OH (DMP 18)	322.1-312.1
77	o dime NH_2 me p C_4 ϕ OH (DMP 14)	322.1-312.1
78	cyclohexylamine	131.0
79	α naphthylamine	121.0
80	β naphthylamine	121.0
81	N me aniline	211.0-221.0
82	N et aniline	221.0-211.0
83	et benzyl aniline	321.0-311.0
84	et p amino benzoate	121.5
85	piperidine	241.0
86	tris (OH me) Aminoethane	111.1
87	2 OH 2 (OH me) 1,3, propanediol	014.1
88	tribenzylamine	311.0
89	tri ϕ guanadine	253.0-353.0
90	salicylaldoxime	521.1
91	rhodanine	251.12
92	urea	152.1
93	Hyamine (p diisobutyl phenoxy ethoxy ethyl dimethyl benzyl amm chloride)	411.1
94	quinaldine	341.0
95	lutidine	341.0
96	2 vinyl pyridine	341.07

No.	Name	Class
97	2 me 6 amino pyridine	342.0-142.0
98	N β OH propyl-o toluidine	221.1-211.1
99	aminohydroquinone diet ether	131.17
100	aminohydroquinone di me ether	131.17
101	φ carbethoxy pyrazolone	332.57-232.57
102	NN di β OH ethyl-m toluidine	311.1-321.1
103	octadecenyl dimethylamine	311.07
104	tribenzylamine (Advance)	311.0
105	N et N β OH ethyl aniline	311.1-321.1
106	NN di β OH et aniline	311.1-321.1
107	Schiff's base (NN' disalicylalen.)	312.17
108	Iminodipropionitrile	513.07-213.07
109	ββ' oxydipropionitrile	512.17
110	Thiodipropionitrile	512.27
111	di me ethanolamine	311.1
112	di et ethanolamine	311.1
113	me diethanolamine	311.1
114	ethyl morpholine	341.1
115	2 me 5 et pyridine	341.0
116	diethylene triamine	213.0-113.0
117	methyl benzyl diethanolamine	311.1
118	acetoacet-o-anisidide	221.5-251.5
119	dibutyl dithiocarbamate (Butasan)	211.2-511.2
120	Quaternary O Alrose	412.3
121	Quaternary S	412.3
122	Quaternary C	412.3
123	Dry-it Drier (Hurst Plastics Co.)	
124	Activ-8 (in butanol)	342.0
125	Antioxidant B (Nat. An.)	
126	Chlorophyll, alc. sol.	
127	Amine 220 1-OHEt 2 C_7 Decanyl Glyoxalidine	342.17
128	Aminoguanadine	154.0-254.0
129	2 Amino 2OHme 1-3 Propanediol	111.1
130	2 Amino 2 me 1,3 Propanediol	111.1
131	2,5 Di t Butyl Quinone	030.1
132	Dicyandiamide	154.07
133	Diethylene Triamine	113.0-213.0
134	Dime aminome phenol DMP10	311.1
135	Dimethyl Benzylamine	111.0
136	Diphenyl Guanadine	223.07-253.07
137	Ethylene Diamine	112.0
138	Ethyl Morpholine	341.1-311.1
139	Hippuric Acid	211.5-251.5
140	N β OH Propyl o Toluidine	211.1-221.1
141	Methyl Benzyl Diethanolamine	311.1
142	Paracol 7	
143	N φ Morpholine	341.1-321.1
144	β Resorcylic Acid	022.15
145	Sulfanilic Acid	121.12
146	Thialdine	
147	Triphenylamine	321.0

No.	Name	Class
148	acetoacetanilide	221.5-251.5
149	acetoacet-o-chloranilide	221.35-251.35
150	acetoacet-o-toluidide	221.5-251.5
151	NN' disalicylalorthophenylenediamine	322.0
152	NN' dibenzalethylenediamine	312.0
153	NN' dibenzalorthophenylenediamine	322.0
154	NN' disalicylalpropylenediamine	312.1
155	Thiotax	
1G	glycine	111.5
2G	l tyrosine	111.15
3G	dl alanine	111.5
4G	l cystine	112.52
5G	dl methionine	111.52
6G	l glutamic acid	111.5
M-1	Fluid OS-16	
M-2	Santolene C	
M-3	Formulation #9	
M-4	Formylacetanilide thiosemicarbazone	212.27-312.27
M-5	2(2 dimethylamino-ethylamino) pyridine	343.0-213.0-313.0
1H	dibenzenesulfonamide	251.2
2H	N lauryl sulfonyl benzenesulfonamide	251.2
3H	polyamine 1200	21n.0
4H	Benzenesulfonylurea	252.25-152.25
5H	N,3 dimethyl isoquinolinium methosulfate	421.12
6H	N dicyanoethylbenzenesulfonamide	253.2-553.2
7H	Laurylpyridinium chloride	441.3-411.3
8H	N carboxymethyl-3-methylpyridinium chloride	441.35-411.35
9H	Cyanoethyltrimethylamm. methosulfate	411.25
10H	2,2,6,6,tetracyanoethyl cyclohexanone	514.5
11H	2 benzoyl 1 cyano 1,2 dihydroisoquinoline	342.5-542.5

(see p. 30)

- Copy -

APPENDIX III

DRYING TIME TERMS
FEDERAL SPECIFICATIONS
April 18, 1950

---

1) DUST FREE--When the finger, without pressure, can be run over the surface of the paint without picking up any paint on the finger. The surface shall be reasonably hard and non-fluid. While the surface may be sticky, no pronounced marks shall be left by the finger.

2) SET TO TOUCH--When gentle pressure of the finger shows a tacky condition, but none of the coating adheres to the finger.

3) TACK FREE--A film shall be considered tack free when the finger with a slight pressure will not leave a mark. The surface shall not be sticky.

4) DRIED HARD--When the maximum pressure that can be exerted between the thumb and finger (without twisting) does not move the film nor leave a mark which remains noticeable after the film is lightly polished.

5) FREE FROM AFTER TACK--When on the above test, for dried hard, exerted for a maximum of 2 seconds, the film shows no pull on the thumb.

6) DRY TO HANDLE--When the film cannot be imprinted by maximum pressure of the thumb applied in a rotary manner.

7) FULL HARDNESS--When the film is very difficult to remove with the fingernail and shows excellent resistance to a knife edge.

Drier Department/MTP (Harshaw Chemical Co.)

2-28-51
C

(see p. 30)

APPENDIX IV

Standard Specifications for Raw Linseed Oil

A.S.T.M. Designation: D 234-48

Adopted 1927, Revised 1928, 1948

Scope

1. These qualifications cover raw linseed oil.

Properties

2. Linseed oil shall be the pure oil pressed from flaxseed and shall conform to the following requirements:

Sp. Gr., 15.5/15.5°C.	0.931 to 0.936
Acid number, max.	4.0
Saponification numbers	189.0 to 195.0
Unsaponifiable matter, max.	1.50%
Iodine number (Wijs), min.	177
Loss on heating at 105 to 110°C.	0.3, max.%
Appearance	clear and transparent at 65°F.

Color - not darker than a freshly prepared solution of 1.0 g. of $K_2 Cr_2 O_7$ in 100 ml. of pure (H_2SO_4) (sp.gr. 1.84)

Foots, max., percent:

Heated Oil	1.0
Chilled Oil	4.0

Methods of testing

3. The properties enumerated in these specifications shall be determined in accordance with the Standard Methods of Testing Drying Oils, (A.S.T.M. Designation 555).

(see p. 33)

APPENDIX V

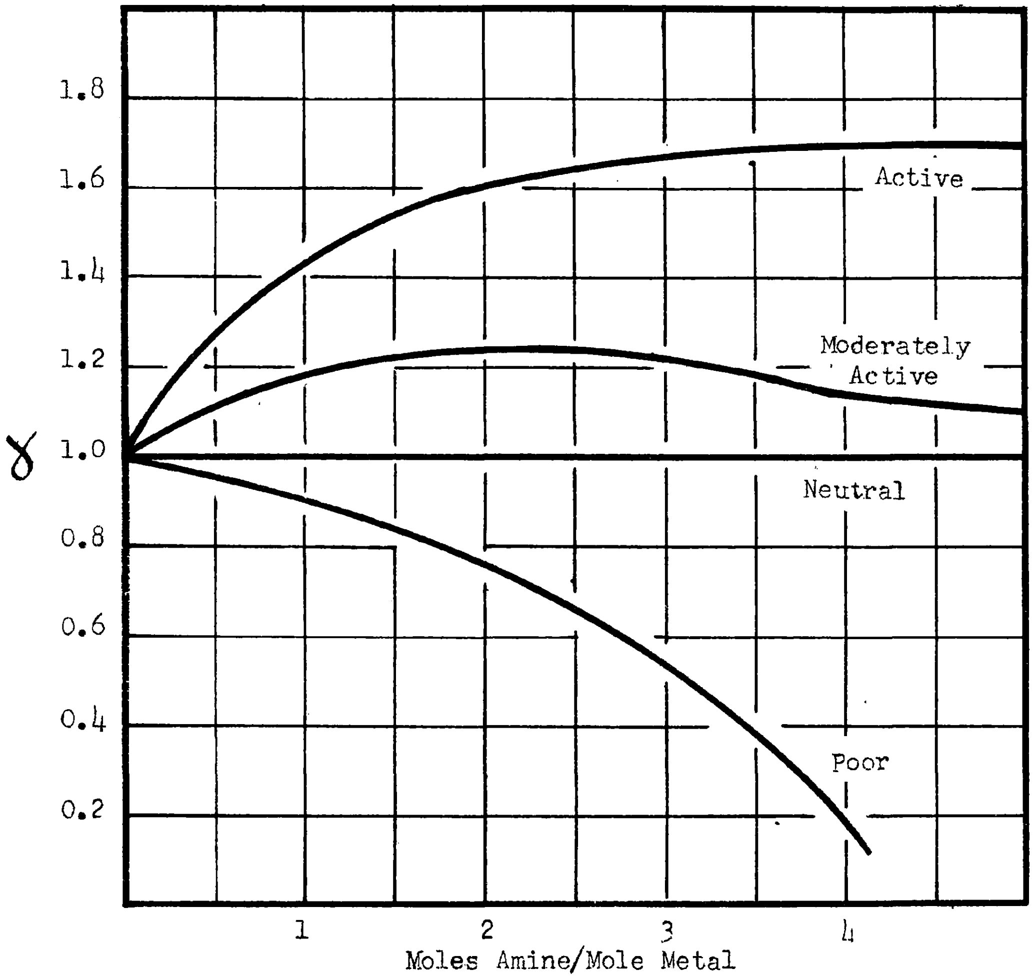

Figure 8

Effect of Amine Concentration on Evaluation Results

See Page 37

G.E.
4/8/52

APPENDIX VI

Acceleration of Manganese Catalysis by Schiff's Base (NN' disalicylalethylenediamine)

Aging studies of the effect of Schiff's base in eleven vehicles resulted in Figures 10-21 which follow. The behavior of orthophenanthroline when cast in the same role is shown in Figure 22.

The curves which comprise the next eleven pages were obtained by averaging the values of all the manganese concentrations; otherwise, over 50 curves would have resulted. The ordinate, γ, can be translated into percentage improvement by subtracting 1.00, since it is $\gamma_{0.05Mn}$. The abscissæ are the mole ratio of amine to metal. See pages 48 and 49 of text.

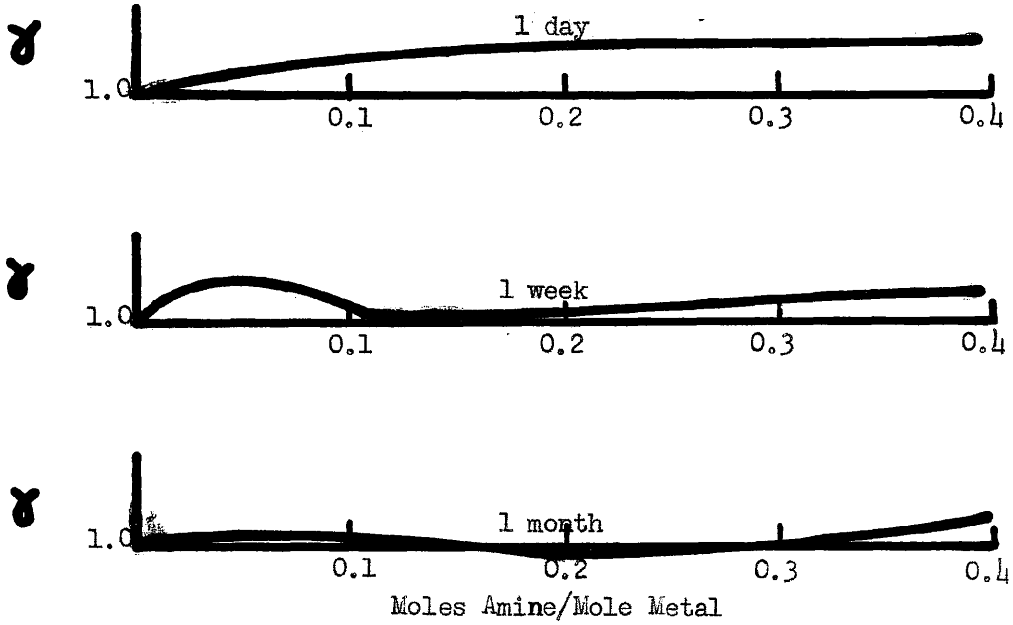

Figure 10. Vehicle A-1

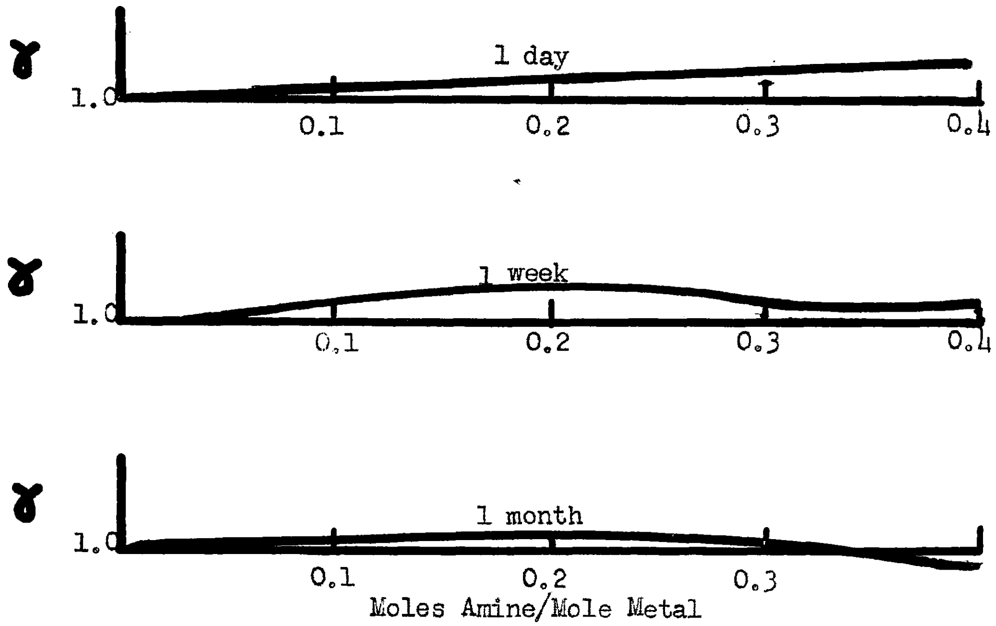

Figure 11. Vehicle A-2

CEM
4/17/52

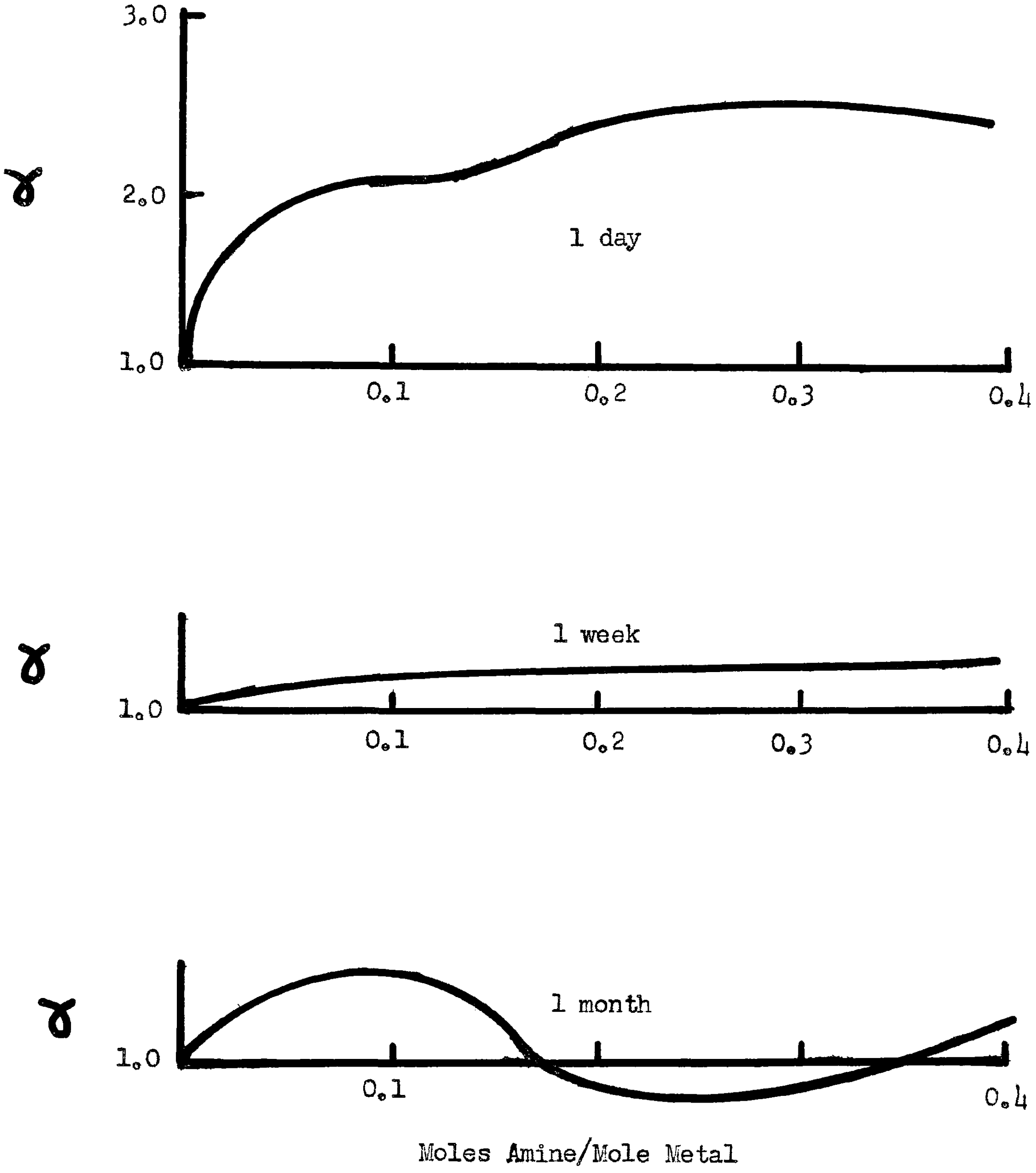

Figure 12. Vehicle A-3

CEM
4/17/52

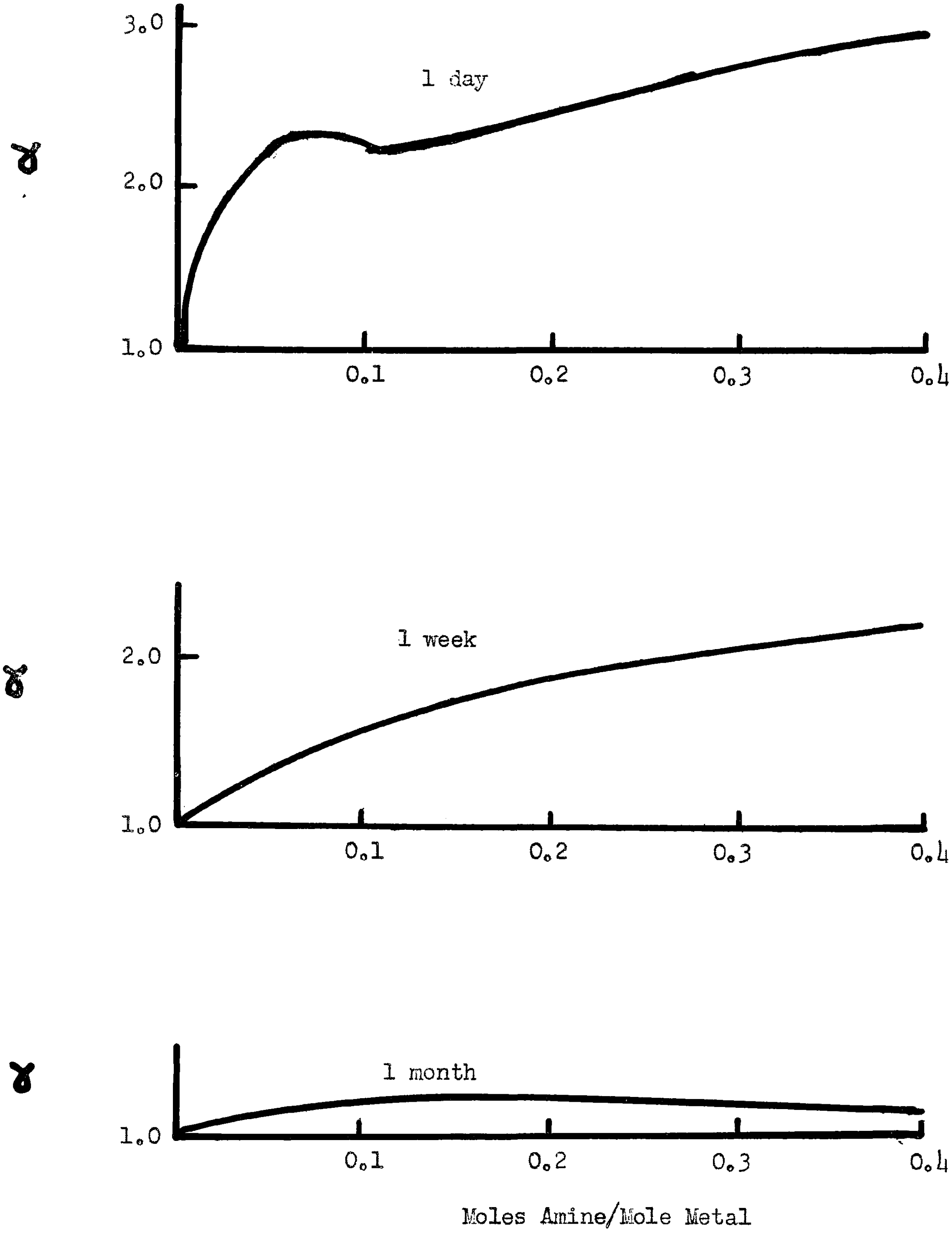

Figure 13. Vehicle A-4

CEM
4/17/52

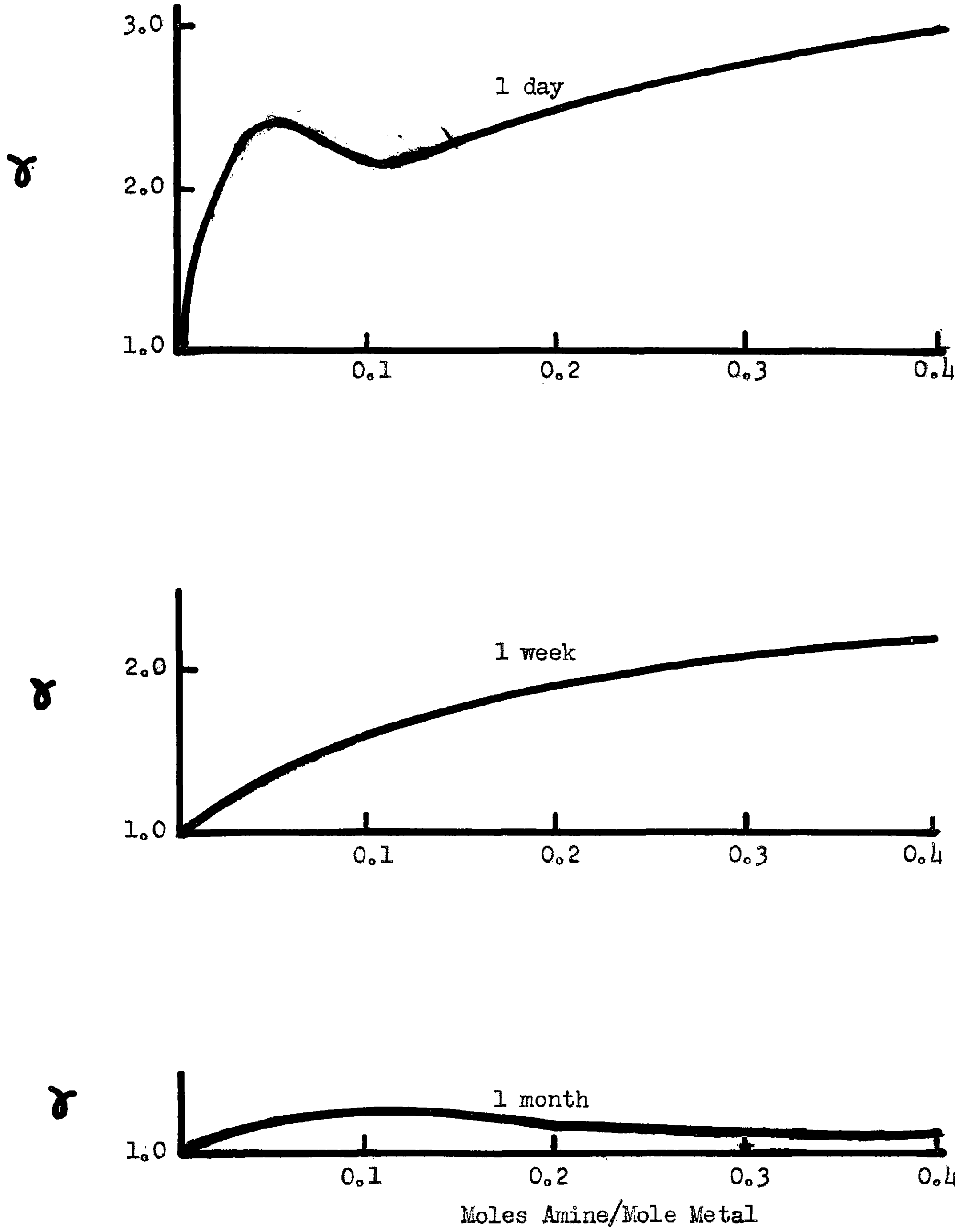

Figure 13. Vehicle A-4

CEM
4/17/52

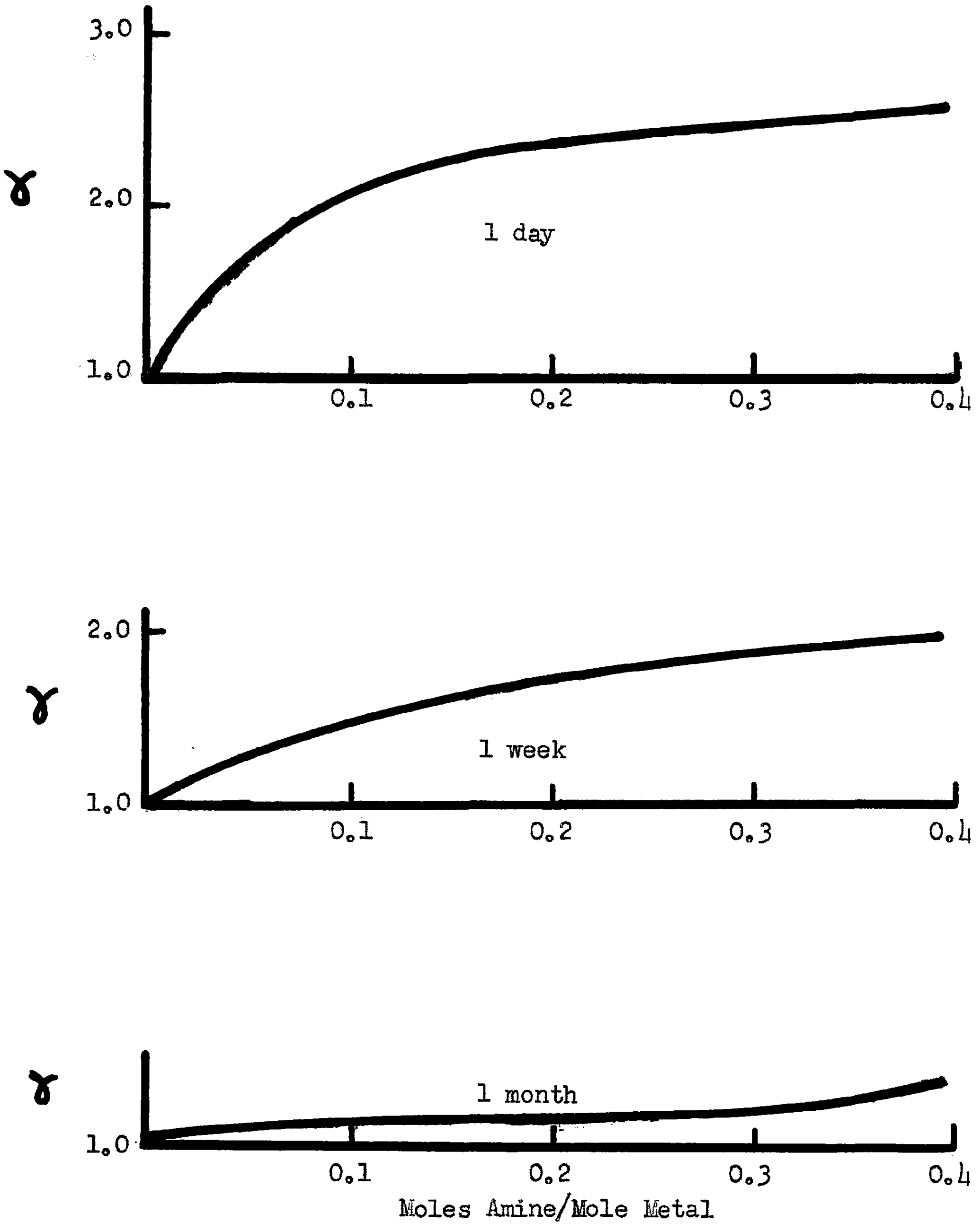

Figure 14. Vehicle A-5

CEM
4/17/52

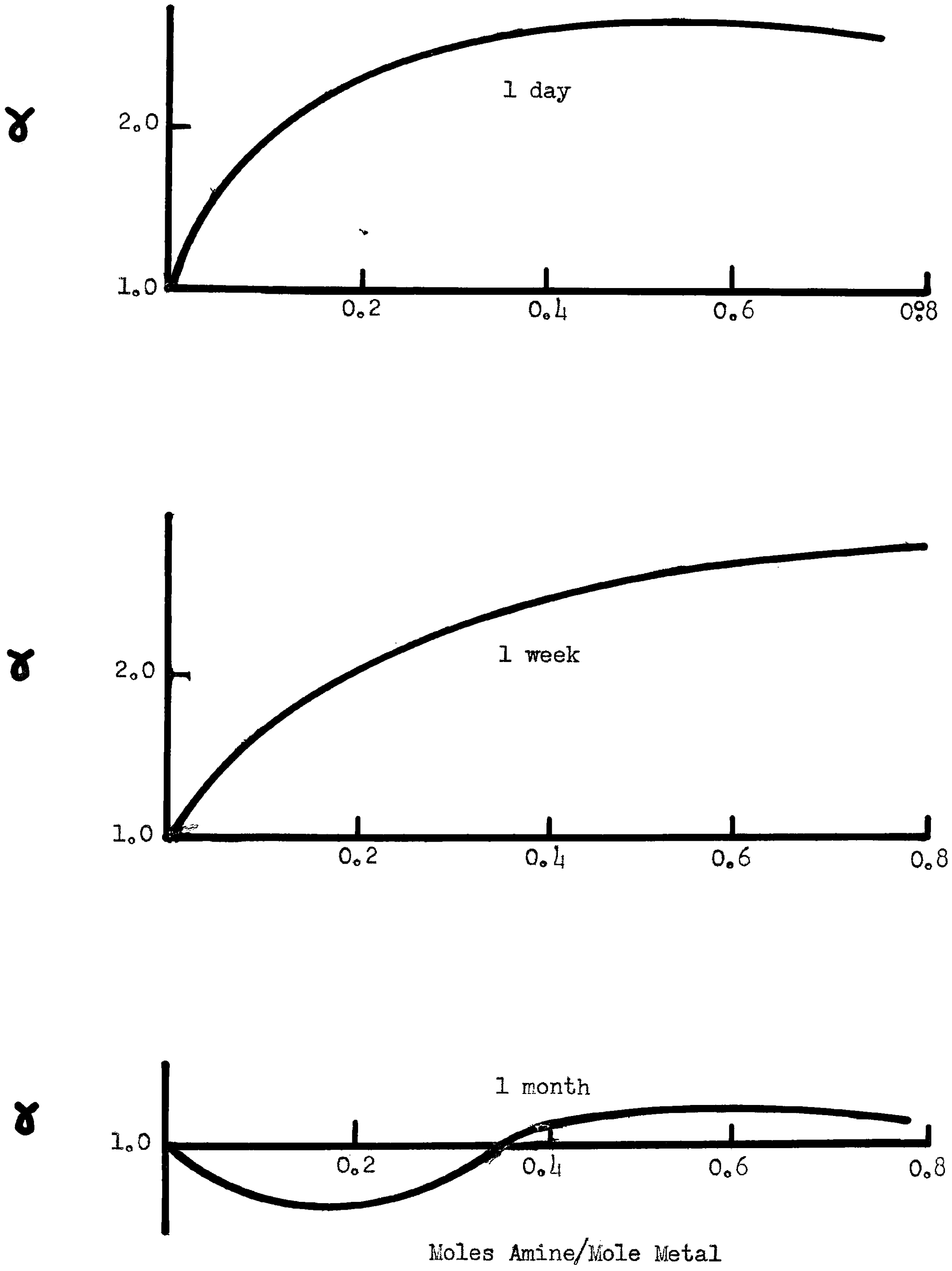

Figure 15. Vehicle B-1

CEM
4/17/52

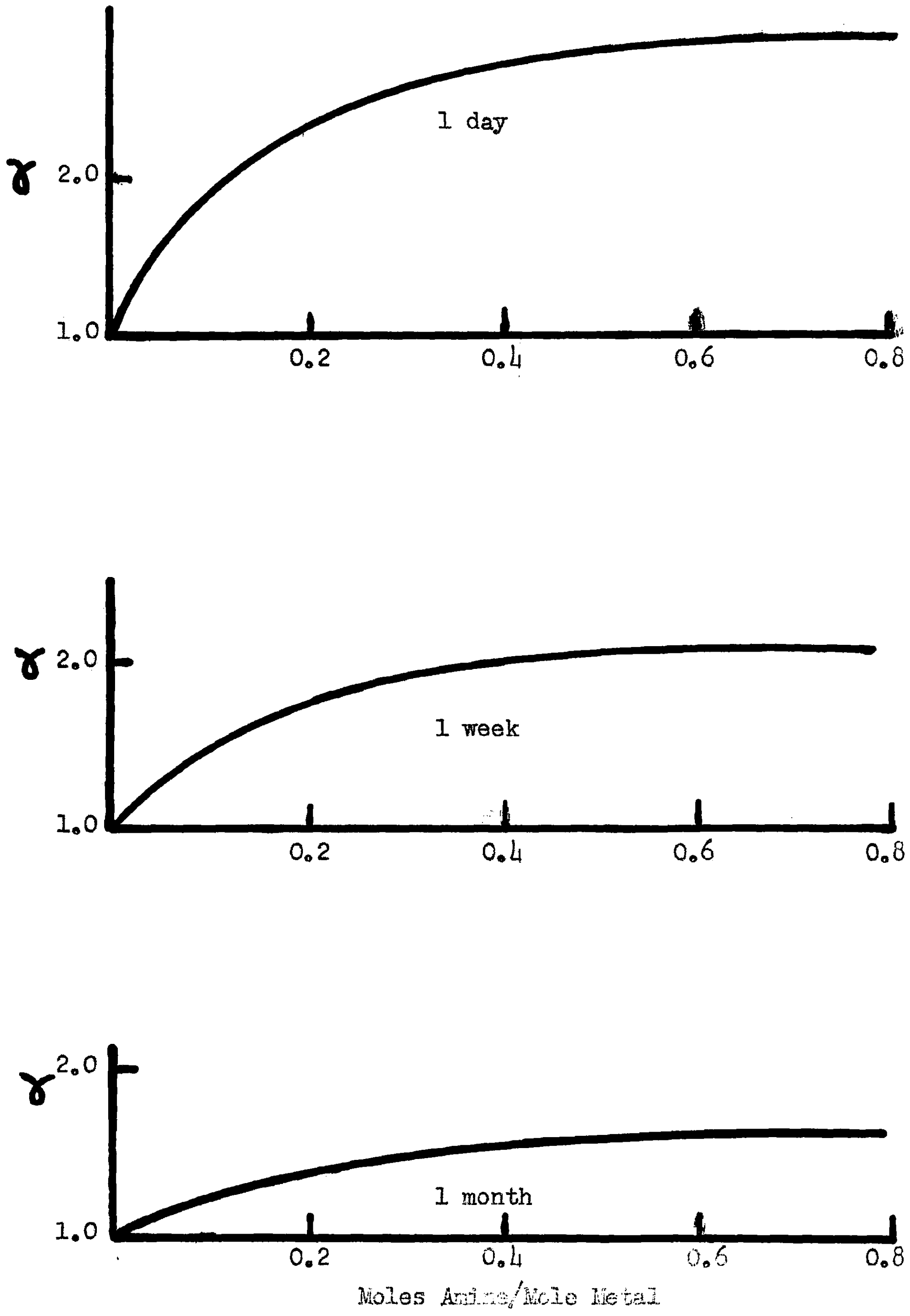

Figure 16. Vehicle B-2

CEM
4/17/52

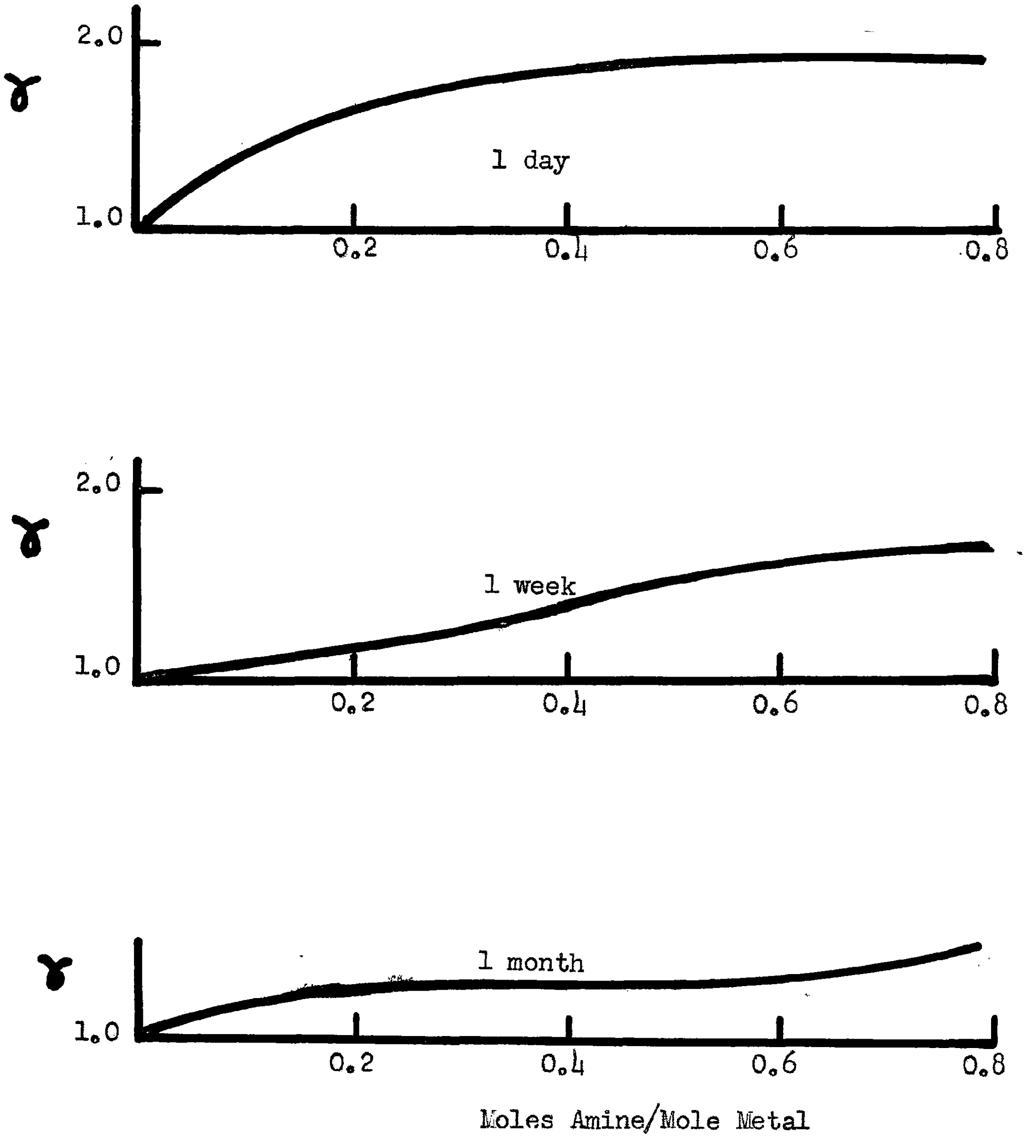

Figure 17. Vehicle B-3

CEM
4/17/52

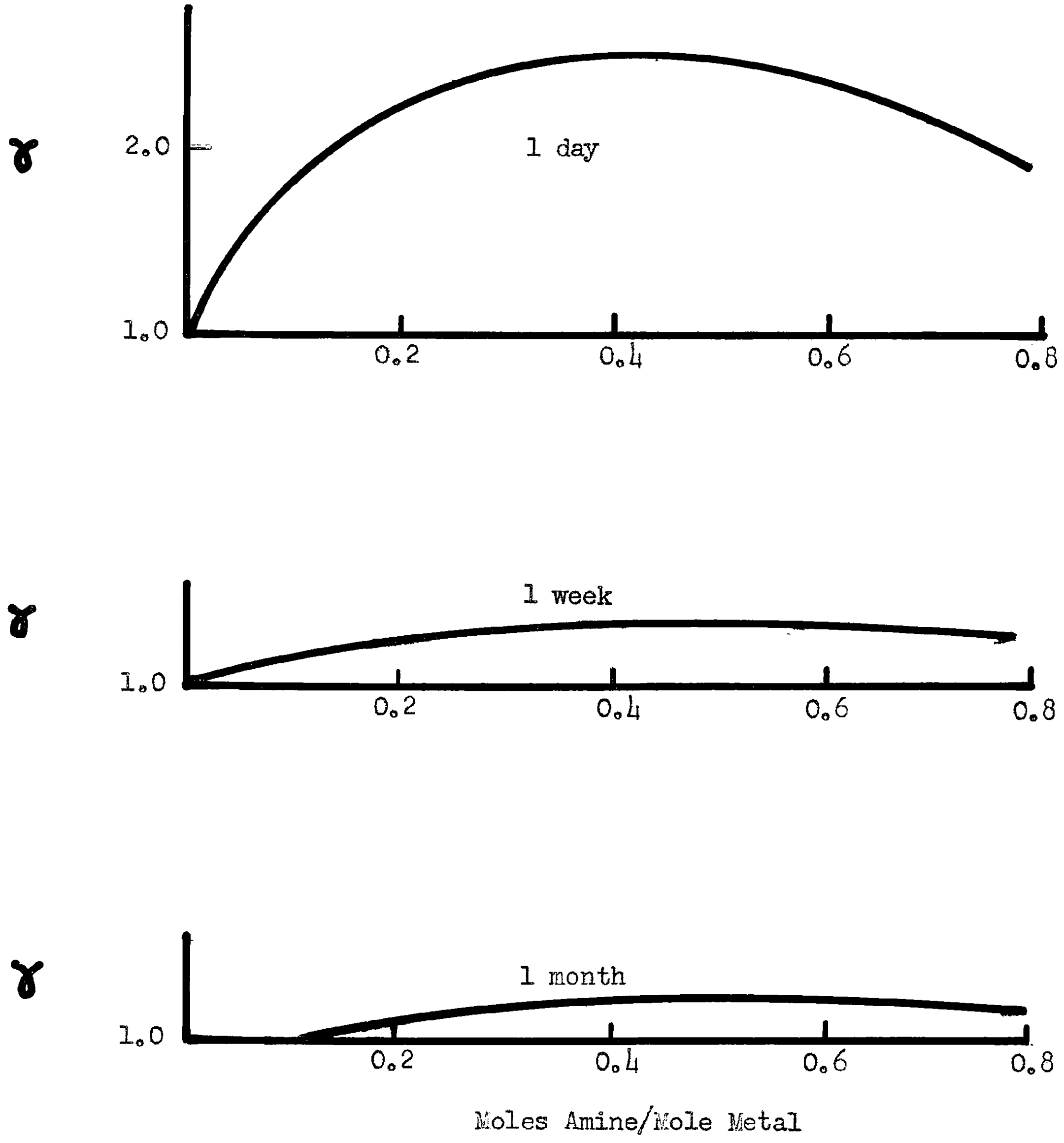

Figure 18. Vehicle B-4

CEM
4/17/52

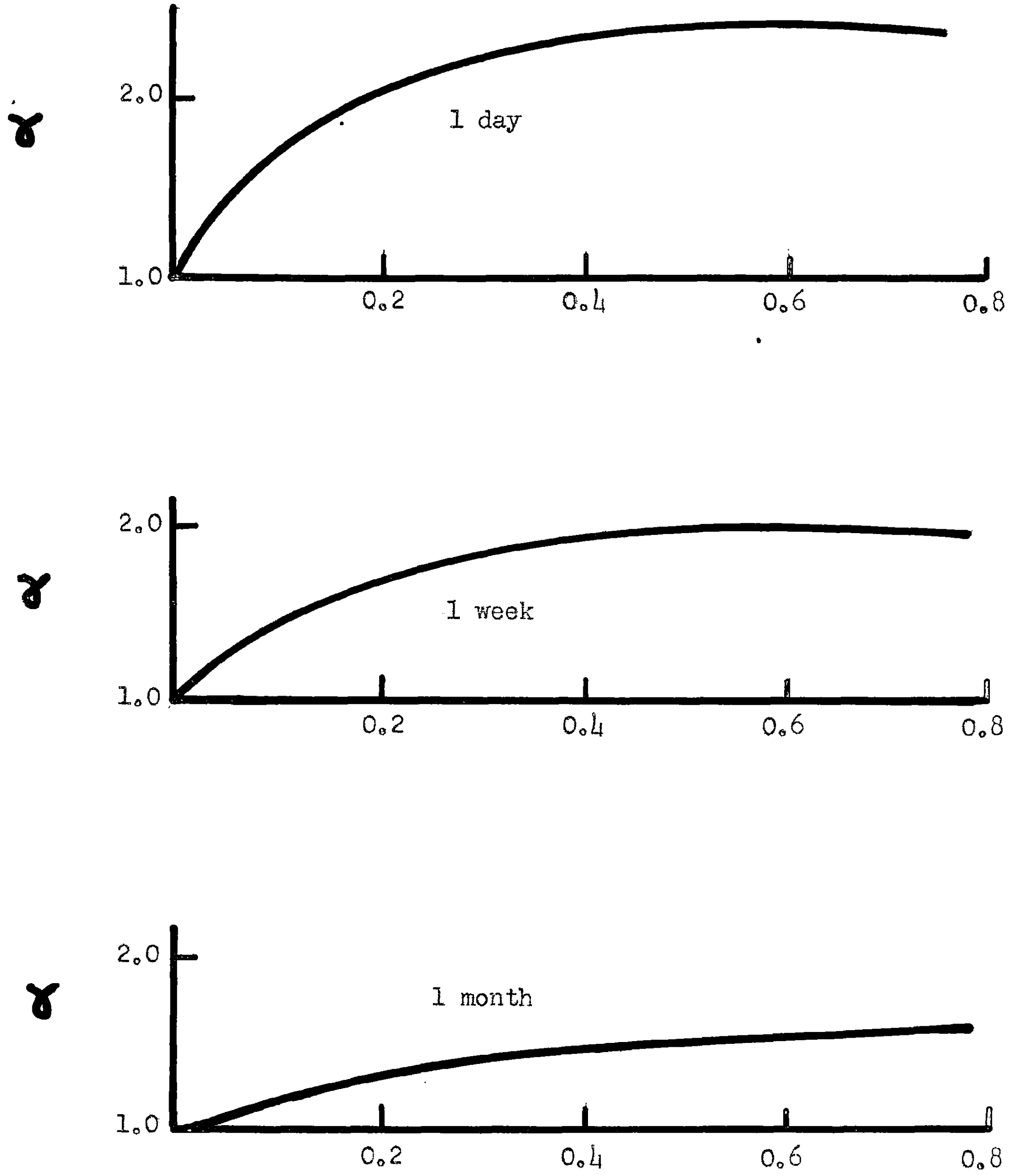

Figure 19. Vehicle B-5

CEM
4/17/52

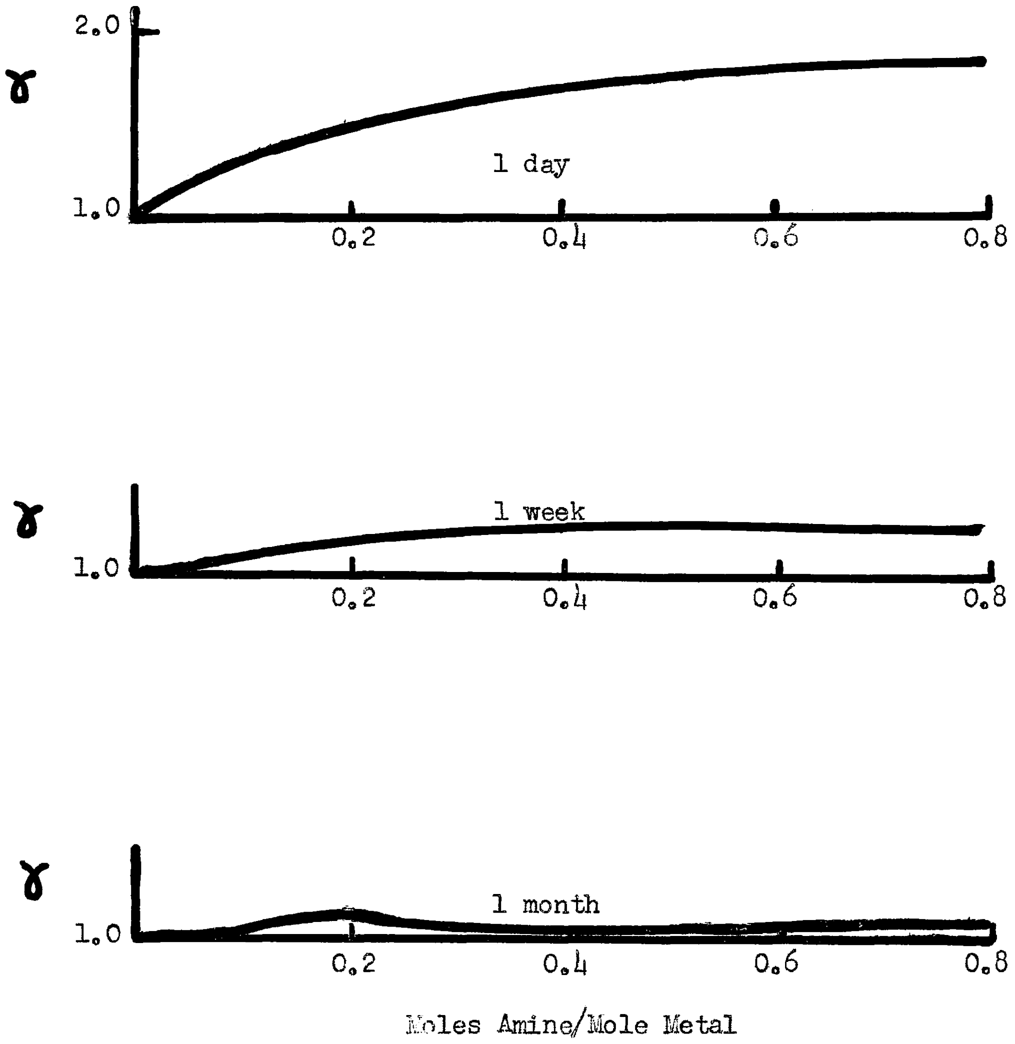

Figure 20. Vehicle B-6

CEM
4/17/52

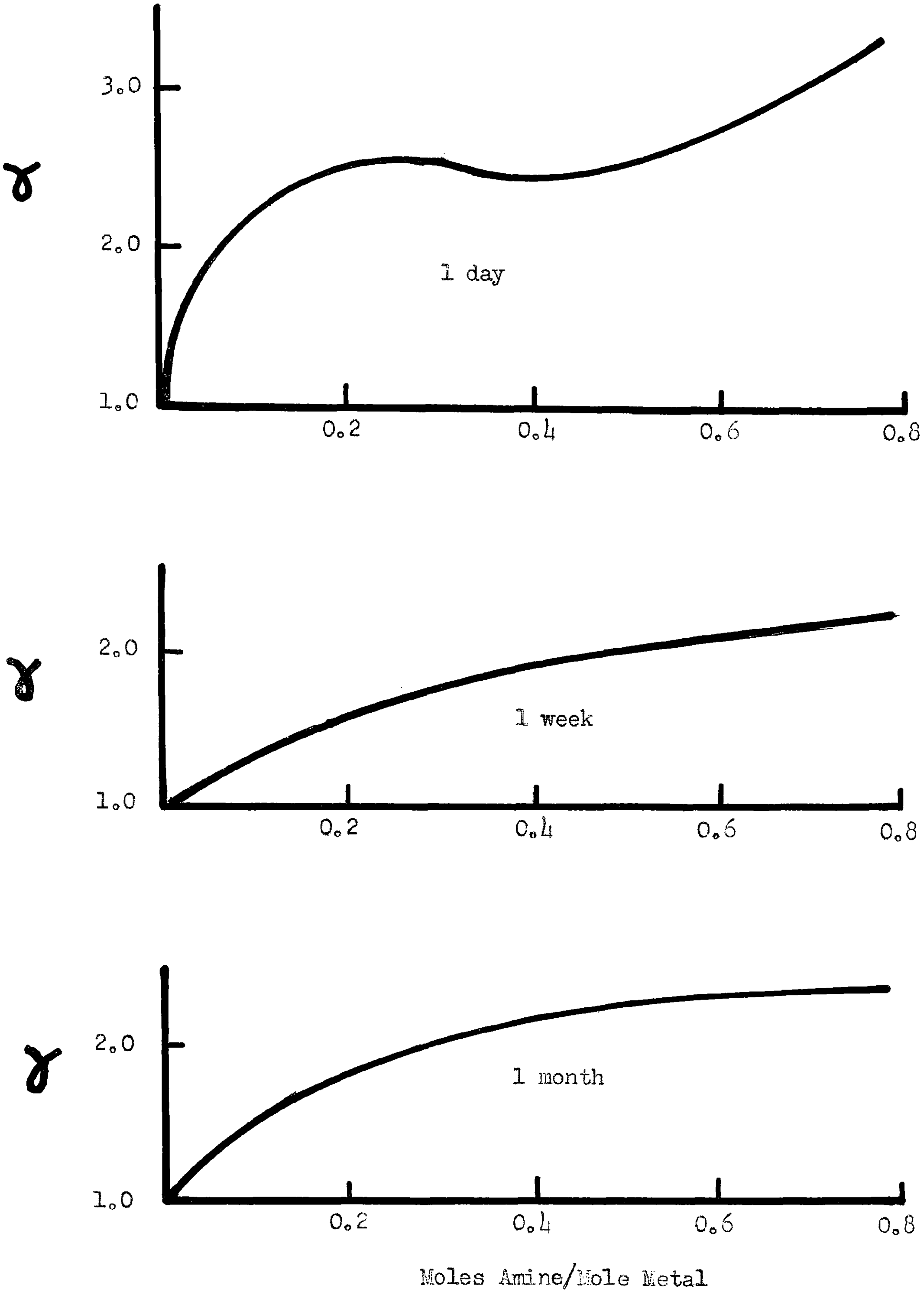

Figure 21. Ortho Phenanthroline in Vehicle B-1

CEM
4/17/52

APPENDIX VII

Cost Estimate on Use of Schiff's Base

This estimate is based on prices listed in recent editions of *Chemical and Engineering News* for the following:

Metallic cobalt	at	\$2.40 per lb.
Metallic manganese	at	0.30 per lb.
Ethylenediamine	at	0.63 per lb.

and by direct quotation from the Dow Chemical Company:

Salicylaldehyde	at	1.25 per lb.

……

Basis: 100# varnish Assumption: 0.03%Mn (complexed)
=0.03%Co (uncomplexed).

Catalyst Cost:

CASE I: 0.03% Co = 0.03# Co

0.03# x \$2.40/# = 7.2¢ (cost of drier)

CASE II: 0.03% Mn = 0.03# Mn

0.03# x \$0.30/# = 0.9¢ (cost of drier)

CASE III: 0.03% Mn + 0.05 moles Schiff's base/mole metal

= 0.03# Mn + $\frac{0.03}{55}$ x 0.05 = 0.0000275 lb. moles amine

Amine cost = \$342.80 per lb. mole

= 0.94¢ per 0.0000275 lb. moles

Metal cost = 0.90¢

Total = 1.84¢

Savings = 5.36¢ = 74.5%

CASE IV: 0.03% Mn + 0.10 moles Schiff's base/ mole metal

= 0.03# Mn + 0.000055 lb. moles amine

Amine Cost = 1.88¢

Metal Cost = 0.90¢

Total = 2.78¢

Savings = 4.42¢ = 61.5%

CASE V: 0.03% Mn + 0.15 moles Schiff's base/ mole metal

= 0.03# Mn + 0.0000825 lb. moles amine

Amine Cost = 2.83¢

Metal Cost = 0.90¢

Total = 3.73¢

Savings = 3.47¢ = 48.3%

……

Savings at Various Molar Ratios:

Moles Amine / Mole Metal	0.0	0.05	0.10	0.15	0.20	0.30	0.40
% Savings	87.5	74.5	61.5	48.3	35.2	9.0	-17.2

(see p. 52)

APPENDIX VIII

Bjerrum's Method

If ammonium hydroxide and an ammonium salt are added to a solution of a metal salt, the number of bound ammonia molecules which coordinate can be found by a) measuring the hydrogen ion concentration, or the pH; b) calculating the concentration of free ammonia in solution by the relationship,

$$NH_3 + H^+ \rightleftarrows NH_4^+ ,$$

(since NH_4^+ can be assumed equal to the ammonium salt concentration); c) calculating the bound ammonia by subtracting the free ammonia from the total ammonia (which equals the concentration of ammonium hydroxide*); and d) computing the average number of bound ligands per metal ion from the concentration of the metal salt.

The importance of this method lies in the fact that the ammonia tension is not measured; instead, the accuracy and extremely wide range of the glass electrode is exploited**.

---

* More precisely: the ammonium hydroxide plus the hydrogen ion concentration.

** A p^H range of 14 units gives a p^A range of equal magnitude, or a 1×10^{14} concentration range.

(see p. 89)

APPENDIX IX

Kf Values for Selected Organic Solvents

Kf	Substance	M.P
37.7	camphor	178
20.4	tribromophenol	96
20.0	cyclohexane	6.5
14.4	bromoform	7.8
12.5	ethylene dibromide	10
12.45	tri Ø methane	93
12.3	salol (Ø salicylate)	43
12.0	phenanthrene	99
11.25	β naphthol	122
10.6	m dinitrobenzene	90
9.8	benzophenone	48
8.6	di Ø amine	53
8.1	nitrobenzene	5.7
8.0	diphenyl	70
7.27	phenol	42
6.9	naphthalene	80
5.12	benzene	5.5
4.9	1,4 dioxane	10.5

(see p. 96)

APPENDIX X

- Copy -

THE EPPLEY LABORATORY, INC.
Newport, R. I.

CALIBRATION
OF MUELLER
TEMPERATURE BRIDGE

Serial No. 301

At Temperature of 25.0°C. ± 0.1°

Dial Reading	Correction	Dial Reading	Correction	Dial Reading	Correction
10 ohm Dial		1 ohm Dial		.1 ohm Dial	
10	+ .00054 Ω	1	+ .000062 Ω	.1	+ .000044 Ω
20	+ .00108	2	+ .000087	.2	+ .000090
30	+ .00139	3	+ .000102	.3	+ .000134
40	+ .00173	4	+ .000164	.4	+ .000178
50	+ .00204	5	+ .000214	.5	+ .000218
60	+ .00243	6	+ .000264	.6	+ .000264
70	+ .00274	7	+ .000326	.7	+ .000283
80	+ .00308	8	+ .000388	.8	+ .000289
90	+ .00332	9	+ .000438	.9	+ .000320
100	+ .00356	10	+ .000513	1.0	+ .000339
.01 ohm Dial		.001 ohm Dial		.0001 ohm Dial	
.01	+ .000023 Ω	.001	+ .000018 Ω	.0001	±.000000 Ω
.02	+ .000009	.002	+ .000024	.0002	±.000000
.03	+ .000020	.003	+ .000032	.0003	-.000013
.04	+ .000018	.004	+ .000038	.0004	-.000013
.05	+ .000016	.005	+ .000031	.0005	-.000013
.06	+ .000027	.006	+ .000024	.0006	-.000013
.07	+ .000025	.007	+ .000042	.0007	-.000003
.08	+ .000037	.008	+ .000035	.0008	-.000003
.09	+ .000023	.009	+ .000016	.0009	-.000003
.1	+ .000021	.01	+ .000022	.001	+.000007

The above corrections are to be applied to the dial readings indicated in accordance with their signs.

Newport, R. I.
Oct. 30, 1931

In Charge of Test.
William R. Gray

(see p. 100)

APPENDIX XI

Table XXIV

REACTIVITY OF VARIOUS AMINES WITH COBALT ACETATE

Amine	Reactivity
n Propylamine	Complete. Violet Solution
di n Propylamine	Complete. Violet Solution
Cyclohexylamine	Violet solution. Pink sludge.
Triamylamine	No apparent reaction.
Stearyl dimethylamine	Slight reaction.
NN'diethyl cyclohexylamine	No apparent reaction.
DMP 14	Considerable. Dark red solution.
DMP 30	Complete. Red solution.
Ethylbenzylaniline	No apparent reaction.
Ethyl Morpholine	Little or none.
Diethylene Triamine	Yellow solution. Pink sludge.
2(2 dimethylaminomethylamino) pyridine	Complete. Violet solution.
p Octadecenyldimethylamine	Little or none.
Orthophenanthroline	Colorless solution. Brown solid.
Piperidine	Violet solution. Bluish sludge.
Triphenylguanadine	Slight reaction.
Thialdine	No apparent reaction.
Hexamethylenetetramine	No apparent reaction.
NN' disalicylalethylenediamine	Olive solution. Dark sludge.

Criterion of reactivity: appearance of color in the solution combined with change in appearance or amount of the solid.

(see p. 104)

APPENDIX XII

Temperature-Resistance Relationship of Thermistor Assembly

The resistance of a semiconductor of the thermistor variety is expressed:

$$R_t = R_{\infty} e^{\frac{B}{T}} ;$$

while the resistance of the auxiliary manganin resistor is constant:

$$R_a = k ,$$

and the resistance of the solution in which the thermistor is immersed is infinite in the cases studied:

$$R_s = \infty .$$

The total resistance of the assembly consisting of R_a, R_t and R_s in parallel is

$$\frac{1}{R} = \frac{1}{R_a} + \frac{1}{R_t} + \frac{1}{R_s} = \frac{1}{k} + \frac{1}{R_{\infty}} e^{-\frac{B}{T}}$$

When k is infinite the equation reduces to that of the thermistor. When k is small, the characteristics are more nearly those of a straight line, approaching zero slope as a limit.

The near-linearity of the relationship is shown in Appendix XIII (Figure 28).

(see p. 107)

(see p. 107)

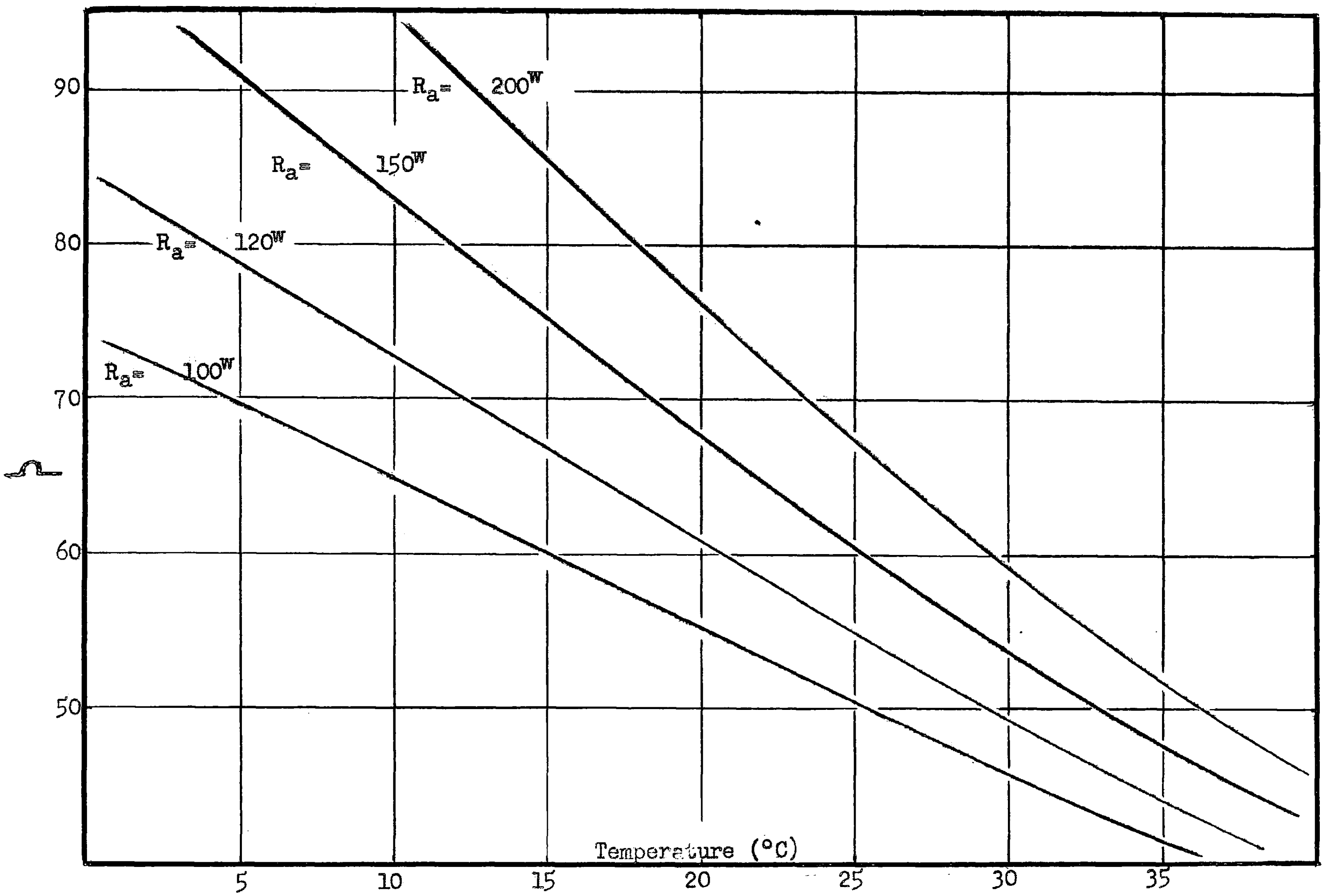

Figure 28. Temperature Characteristics of Thermistor Assemblies

APPENDIX XIV

Record of Original Data

SUBJECT	Notebook amd Page Numbers (Metal Complex File)
Cryoscopy	I: 215-297; II: 128-129; III: 82, 144-6
Silver acetate	I: 247-253; II: 128-129; III: 82, 144-6
Cobalt acetate I	I: 215-226
Cobalt acetate II	I: 290-297
Manganese chloride	I: 284-289
Amine Evaluation	I: 15-86, 228-264; II: 16-152; III: 5-28, 38-60, 65-153; IV: 5-34, 43-63, 68-108
Complex Preparation	I: 23-25, 51-78, 89-93, 99-110, 121-165; III: 34-35; IV: 36-48, 67-79, 88-97
Pyrrolidone Complex	I: 99-100, 123-124, 128-130
Aminoguanadine Complex	I: 137-140, 145-147
Schiff's Base Aging	I: 203-225, 241-249, 254-261; III: 115-153; IV: 6-17, 73-78.

(see pp. 69, 70, 72)

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VITA

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