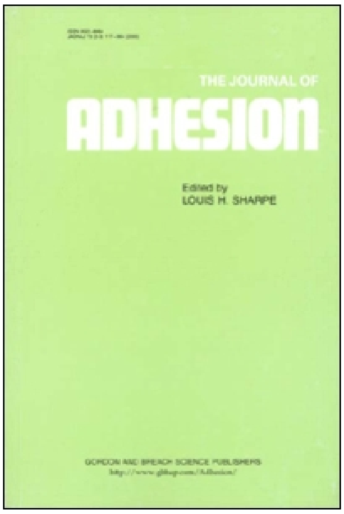

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# Adhesives from *Pinus Radiata* Bark Extractives

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# Adhesives from *Pinus Radiata* Bark Extractives

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Extracts containing tannins and related polyphenols were obtained from *Pinus radiata* bark by extraction with hot water containing small amounts of sodium carbonate and/or sodium sulphite. The extracts had excessive viscosities ($>10$ Pa.s) at the concentrations required for adhesive formulation, but this problem was readily overcome by reducing the pH of the extract solution to below 4.5 with acetic acid, adding a small amount of phenol, and heating the mixture. Adhesive performance was best between pH 4.5–6.0, and the bonds were resistant to boiling water. However, joints bonded with early adhesive formulations tended to fail within the adhesive, necessitating some form of adhesive fortification in later formulations. The results obtained with a number of different additives as fortifiers are presented. Softwood plywood which passed the bond quality requirements of the boiling test described in U.S. Product Standard 1–74 was made in the laboratory using these fortified adhesives.

## INTRODUCTION

In New Zealand, the polyphenols in *Pinus radiata* bark have long been considered as a potential substitute for petroleum-based raw materials in adhesives formulation[1] and recently a New Zealand manufacturer of panel products has initiated their commercial exploitation.[2]

This paper describes some of the results obtained at the New Zealand Forest Research Institute in attempting to make adhesives from *P. radiata* bark extractives. These extractives consist mainly of polyphenols such as tannins and related compounds of various molecular

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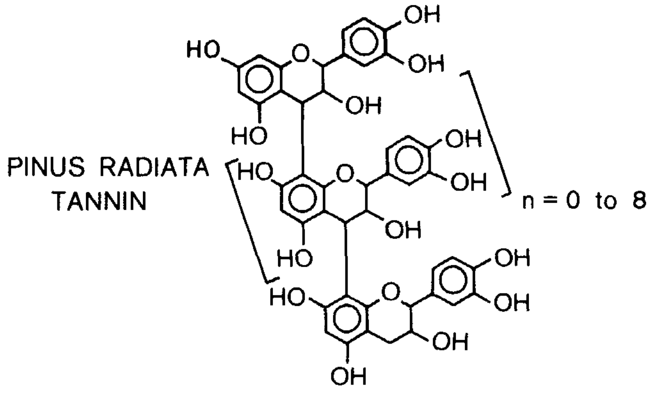

FIGURE 1 Chemical formula of a typical *Pinus radiata* bark tannin.

weights. A molecular structure representative of a *P. radiata* tannin is shown in Figure 1.

In the laboratory, the extracts are readily prepared from hammer-milled, air-dried bark by extraction with hot water containing small amounts of sodium carbonate and/or sodium sulphite.[1,3,4] The filtered extract is concentrated in a climbing film evaporator and the viscosity is reduced by chemical modification. The resulting solution is spray-dried for future use. Reconstitution is achieved by dissolving the the spray-dried extract in water.

The tannins in the extract solutions react rapidly with formaldehyde to form a crosslinked resin. However, the mobility of the tannin molecules in the glueline is inhibited at a low level of formaldehyde crosslinking and further crosslinking is difficult because of the inability of the small formaldehyde molecules to bridge the gaps between reactive sites on the immobilised tannins. To enhance the bonding performance of radiata pine tannin-based adhesives an additional hardener or fortifier, with molecules sufficiently long to bridge the gaps, must be incorporated. The fortifier may be added prior to spray drying the extract or when the adhesive is being mixed. Adhesives thus modified have been used to make plywood with waterproof bonds.

## EXPERIMENTAL

### Preparation of Extracts

Fresh *P. radiata* bark was collected from a mill debarker, air-dried and hammermilled to particles less than 2 mm diameter. The bark was extracted with dilute aqueous solutions of sodium carbonate (0–2.5% by weight of oven dry bark) and/or sodium sulphite (2.5–0% by weight of oven dry bark) at 60–90°C for 10–15 minutes. The liquor to bark ratio was 5 : 1. In some cases the sodium sulphite was added after extraction with sodium carbonate solution. The dilute extract solutions were concentrated to 25–30% solids in a Corning Glassware QVF climbing film evaporator at about 45°C. Further concentration was done using a Buchi rotary evaporator, or the extract solutions were spray-dried.

## Viscosity measurement

Viscosities were measured with a Brookfield Viscometer Model RVT using spindles RV2 and RV3.

## Gelation Time Measurement

Gelation times were measured with a Techne Model GT-4 gelation timer. Paraformaldehyde (8% of extract solids) was added to a 40% aqueous solution of bark extract at 30°C. The gelation time was recorded as the time taken for 75g of the mixture to gel after it was placed in a constant temperature water bath at 90°C.

## Testing of adhesives

Paraformaldehyde (8% of extract solids) and coconut shell flour (37.5% of extract solids) were thoroughly mixed with aqueous solutions of bark extract containing 40% solids. Lap joints of the type described in British Standard 1204:1965:Part 1[9] were prepared from New Zealand silver beech (*Nothofagus menziesii*). Open assembly time was 2 minutes and the test pieces were pressed six at a time at 1 MPa (150 psi) for 7 minutes at 140°C (284°F). No attempt was made to optimize pressing conditions. For each adhesive mix, six test pieces were immersed in cold water for 24 hours and six in boiling water for 6 hours prior to being tested wet in tension shear. Failing loads were recorded for each test piece. To meet the requirements of the Standard, minimum mean failing loads of 2.24 and 3.45 MPa are specified for the boiling water and cold water soak tests respectively.

### Determination of molecular weight distributions

Molecular weight distributions were determined by gel permeation chromatography of acetylated tannins on a Sephadex LH-60 column (450 mm long and 10 mm I.D.) with chloroform as solvent. The tannins were acetylated with acetic anhydride and pyridine by the method of Erman and Lyness.[15] The column was calibrated using acetylated phenols and flavanoids of known molecular weight, and polystyrene standards.

### Plywood manufacture and testing

*Pinus radiata* veneers, 30 cm square by 3 mm thick, were made into 3-ply panels using the adhesive formulation already presented, except that, where applicable, appropriate amounts of the fortifying resins were added. Veneer moisture content was 7–8%, gluespread was 400 g/m$^2$ of double glueline (82 lb/MDGL), and the laid-up panels were left for 10 minutes prior to prepressing for 10 minutes at 1 MPa (150 psi). The panels were hotpressed for 5 minutes at 160°C and 1.2 MPa (175 psi), one panel per press opening.

Each 3-ply panel was cut into 24 shear specimens of the size and shape specified in U.S. Product Standard 1–74.[14] Half of the shear specimens were machined so as to open the lathe checks when subjected to a tensile stress and half so as to close the lathe checks. The shear specimens were boiled in water for 4 hours, heated in an oven at 62°C for 20 hours, and then boiled in water for a further 4 hours (boil-dry-boil treatment) before they were placed in cold water and tested as prescribed in PS 1–74. Wood failures were assessed by two operators independently and the means recorded. A minimum wood failure of 85% is a requirement of exterior quality plywood.

## RESULTS AND DISCUSSION

### Viscosity modification

The high viscosities of *P. radiata* bark extract solutions at the concentrations required for adhesive formulation have been a recurring problem because they give rise to handling difficulties in their use as adhesives. Straight aqueous extracts obtained at low temperatures and, consequently, in low yields have behaved satisfactorily in adhesive mixtures, but the economics of the process demand the higher yields which can be obtained by the use of alkaline extracting chemicals at higher temperatures. In general, increasing the temperature and the pH gives higher yields of extract, but it also results in much higher viscosities. Properties such as excessive viscosity and adhesive performance are affected more by higher pH than by higher temperature.[5]

At around 30% solids, many of the bark extract solutions become unstable and the tannins begin to precipitate from solution. The extract solutions behave thixotropically and they must be stirred constantly to maintain a manageable viscosity. The problem is most marked in the high yield extracts obtained using reagents such as sodium carbonate.

Studies on wattle tannins in South Africa by Pizzi[6] have indicated that high viscosity is caused by carbohydrate gums present in the extracts and by intermolecular associations between tannins and carbohydrates and amongst the tannins themselves. Pizzi[6] added acetic anhydride and phenyl acetate to aqueous extracts to break down the carbohydrate gums and disrupt the molecular associations.

At the Forest Research Institute we adapted this process to the extracts of *P. radiata* bark. The pH of the high yield extracts usually lies within the range 5.5–8.5. Acetic acid is added to reduce the pH to 4.0–4.5 and a small amount of phenol is added. The viscosity is substantially reduced by heating the extract at 90–100°C for 15–30 minutes and the problem of thixotropy is eliminated or considerably alleviated. As a rule of thumb, an increase of 5–10% in the solids content can be achieved at equal working viscosities. The amount of phenol necessary for satisfactory viscosity reduction is very small: 1–2% based on extract solids was shown to be sufficient.

## The effects of viscosity modification on the tannins

Generally, heating tannins in acidic conditions leads to condensation reactions, resulting in the formation of high molecular weight phlobaphene-like compounds, accompanied by a sharp increase in viscosity, not a reduction. Weak acids such as acetic acid are able to cleave the heterocyclic ring of the tannin molecule to form a carbonium ion.[7] The carbonium ion thus formed can react with a nucleophile such as sulphite ion, water, phenol or a tannin molecule. Support for this acid-catalyzed cleavage is shown by the spectra in Figure 2. The increased absorbance at about 460 nm is indicative of the formation of xanthylium salts from the tannins.[8] A necessary first step in this reaction is cleavage of the heterocyclic ring to introduce sufficient flexibility into

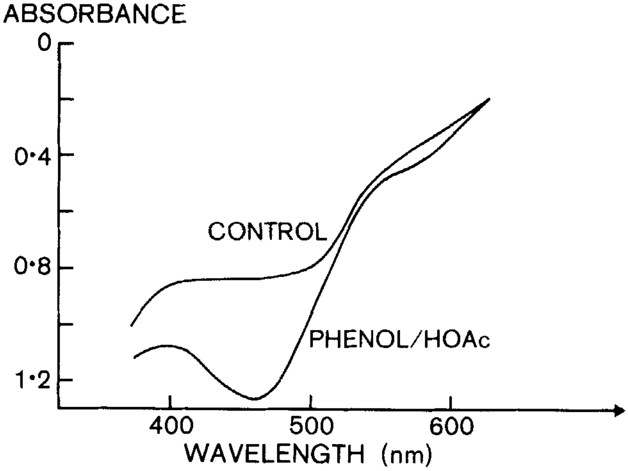

FIGURE 2 The absorption spectra of tannin solutions before and after the phenol/acetic acid viscosity reduction treatment.

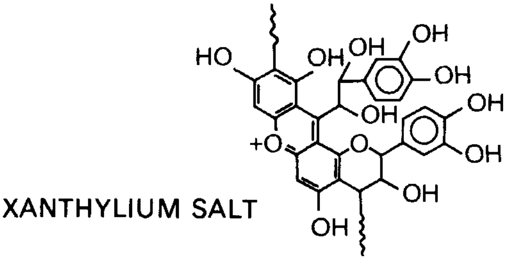

FIGURE 3 The xanthylium salt which can arise from intramolecular rearrangement of a tannin molecule in the presence of acetic acid.

the tannin molecule for intramolecular condensation of the adjacent phenolic hydroxyls and the subsequent formation of the xanthylium salt to take place (Figure 3). Xanthylium salt formation indicates only that the heterocyclic ring is able to be cleaved in the viscosity reduction reaction involving acetic acid and phenol; it does not give a reduction in tannin molecular weight and it is unlikely to contribute to significant viscosity reductions. The importance of the presence of phenol and sulphite ions during the acid-catalyzed reaction lies in their ability to reduce the incidence of intermolecular condensation between tannin molecules by reacting with the carbonium ions.

However, intermolecular condensation of the tannin molecules did

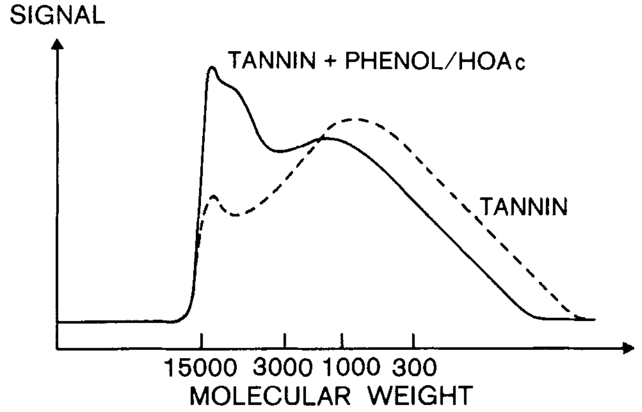

FIGURE 4 The molecular weight distributions of two acetylated tannins, one subjected to viscosity modification with phenol/acetic acid and the other untreated.

occur during the viscosity reduction reaction. Figure 4 shows the molecular weight distributions of two acetylated tannins, one subjected to the phenol/acetic acid viscosity modification reaction and the other untreated. The viscosity-modified tannin had a much greater proportion of high molecular weight tannins, indicative of an intermolecular condensation reaction. Even though the average molecular weight of the tannins increased the viscosity decreased. This supports the theory that carbohydrate gums are the main contributors to high extract solution viscosities, the mildly acid conditions and the application of heat being sufficient to hydrolyze them to lower molecular weight fragments.

## The effect of pH

During development of the viscosity modification procedure using phenol and acetic acid it became apparent that pH had a marked effect on the viscosities of the extract solutions. Figure 5 illustrates the change in viscosity as a function of pH for a viscosity-modified extract. The rapid increase in viscosity above pH 6 made adhesive formulation above this pH difficult.

The effect of pH on adhesive viscosity was even more marked. This resulted from the increasing rate of paraformaldehyde hydrolysis when pH is increased above 4 and the extreme reactivity of formaldehyde with the radiata pine tannins. The high reactivity of the tannins with

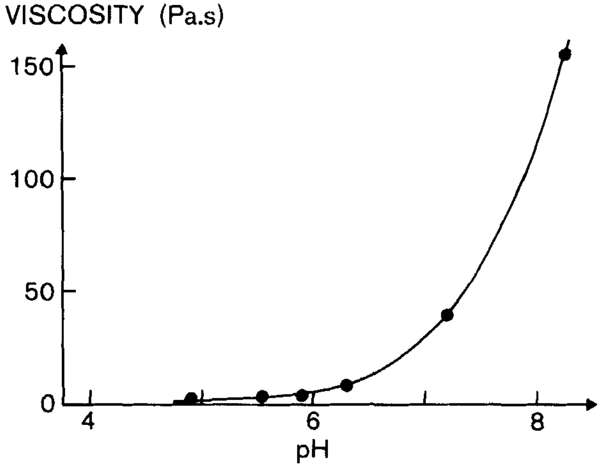

FIGURE 5 Viscosity of a phenol/acetic acid-modified sulphite-carbonate extract as a function of pH.

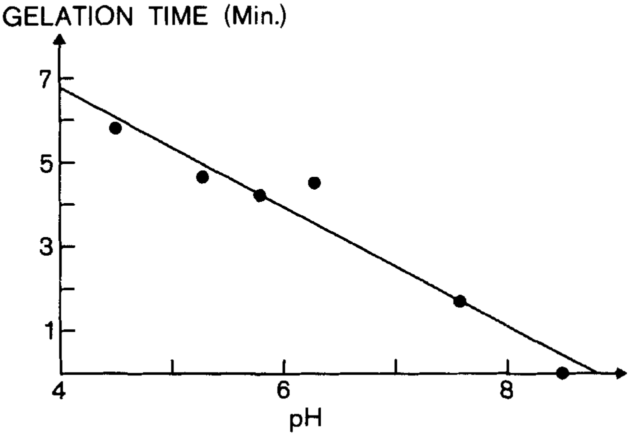

FIGURE 6 Gelation time of a bark extract as a function of pH.

formaldehyde is illustrated by the gelation time measurements at 90°C shown in Figure 6. At pH 8.5 the adhesive gelled almost immediately after mixing.

Over the range considered, optimum bonding, as measured according to the methods of British Standard 1204,[9] was achieved with adhesives

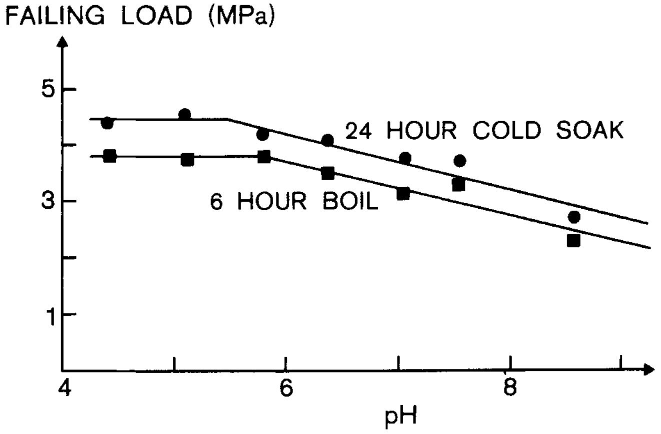

FIGURE 7 Bond quality as measured according to BS 1204 as a function of pH.

of pH between 4.5 and 6.0 (Figure 7). Since viscosity modification works best between pH 4 and 4.5, adhesive pH is generally left at this level.

## Adhesive fortification

Radiata pine bark tannin-formaldehyde adhesives are resistant to boiling water and they give strong bonds with high failing loads. However, failure tends to occur within the adhesive, thus giving rise to low values of wood failure. This would appear to be due to insufficient crosslinking of the tannin molecules by formaldehyde. Larger molecules such as synthetic resin copolymers of phenol, resorcinol or urea with formaldehyde have commonly been used to assist in crosslinking the tannins.[10–12] It has been suggested [13] that the tannin molecules become immobilized at quite low levels of condensation with formaldehyde so that further crosslinking becomes inhibited because of the inability of the small formaldehyde molecules to bridge the distances between the reaction sites on adjacent tannin molecules.

Initially, commercially available resins were tried as fortifiers. Results using a phenol-resorcinol-formaldehyde resin as fortifier are shown in Figure 8. It was not a particularly efficient fortifier. To produce plywood with wood failure exceeding 85% after undergoing the boiling test of U.S Product Standard 1–74,[14] required the addition of more than 40 parts of fortifying resin solids to 100 parts of the extract solids. Thus

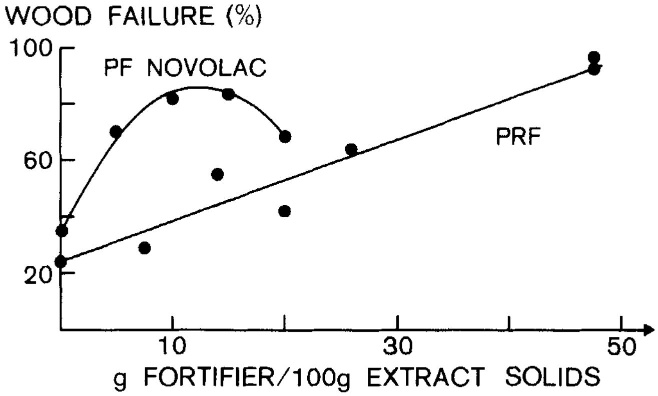

FIGURE 8 Bond quality of plywoods made using tannin-formaldehyde adhesives fortified with a phenol-resorcinol-formaldehyde resin and a phenol-formaldehyde novolac respectively.

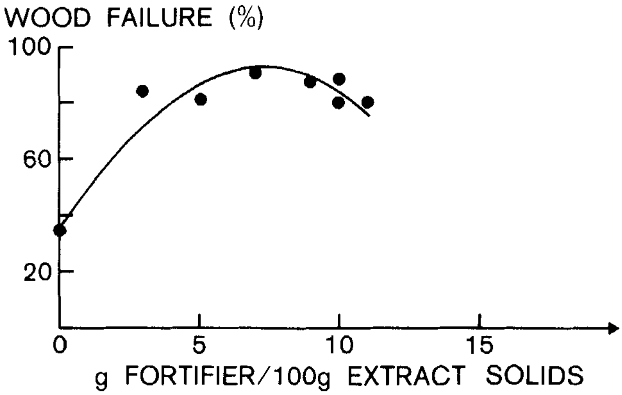

FIGURE 9 Bond quality of tannin-bonded plywoods made with a tannin-phenol copolymer.

the adhesive was more of a resin blend than a fortified tannin-formaldehyde adhesive.

An emulsified isocyanate performed similarly, but it also gave rise to handling problems. The emulsion broke down rapidly in the tannin solutions, evolving carbon dioxide and causing foaming and short pot lives.

To achieve more efficient fortification, a low molecular weight novolac resin was prepared. As shown in Figure 8, high wood failures

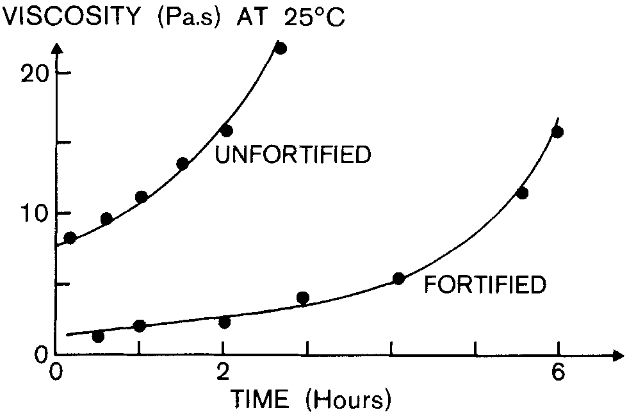

FIGURE 10 The pot lives of tannin-based adhesives with and without incorporated phenols as fortifier.

were achieved when 10–15 parts of fortifier were added to 100 parts by weight of extract solids. Because this resin contains no methylol groups, it does not interact with the tannins in the absence of formaldehyde and it thus forms stable mixtures with the bark extract solutions.

Another approach to tannin fortification was to chemically modify the tannins prior to adhesive formulation by forming tannin-phenol copolymers. The pendant phenolic groups, being readily accessible, lead to easier and increased crosslinking by formaldehyde. The grafting of as little as 3% by weight of phenols on to the tannin molecules gave plywood bonds which passed the boiling test requirements of PS 1–74.[14] (See Figure 9). An advantageous side effect of this system was its tendency to lower the adhesive viscosity and extend the pot life. This is illustrated in Figure 10.

## References

1. R. B. Hall, J. H. Leonard and G. A. Nicholls, *For. Prod. J.* **10**(5), 263 (1960).
2. Anon., *Forest Products News* (New Zealand Forest Products Ltd.) **18**(2), 15 (1981).
3. L. K. Dalton, *Aust. J. Appl. Sci.* **4**, 136 (1953).
4. D. A. Swann, *et al.*, New Zealand Patent 179 933 (11 Feb. 1976).
5. *Building Research 1976*, in CSIRO Australia, Division of Building Research Annual Report, 1976, p. 89.
6. A. Pizzi, *For. Prod. J.* **28**(1), 42 (1978).
7. H. Richtzenain and B. Alfredsson, *Ber.* **89**, 378 (1956).
8. L. Jurd and T. C. Sommers, *Phytochem.* **9**, 419 (1970).
9. British Standards Institution, *BS 1204*, *Specification for Synthetic Resin Adhesives (Phenolic and Aminoplastic) for Wood, Part 1, Close-Contact*, 1965.

10. F. W. Herrick and L. H. Bock, *For. Prod. J.* **8**(10), 269 (1958).
11. K. F. Plomley, J. W. Gottstein and W. E. Hillis, *Aust. J. Appl. Sci.* **15**, 171 (1964).
12. A. Pizzi, *For. Prod. J.* **28**(12), 42 (1978).
13. A. Pizzi, H. Scharfetter and Du T. Rossouw, *Houtim* (CSIR South Africa), No. *52*, 1978.
14. *U.S. Product Standard (PS 1–74) for Construction and Industrial Plywood* (National Bureau of Standards, Washington, D.C.), August 1974.
15. W. F. Erman and W. I. Lyness, *Tappi* **48**, 249 (1965).